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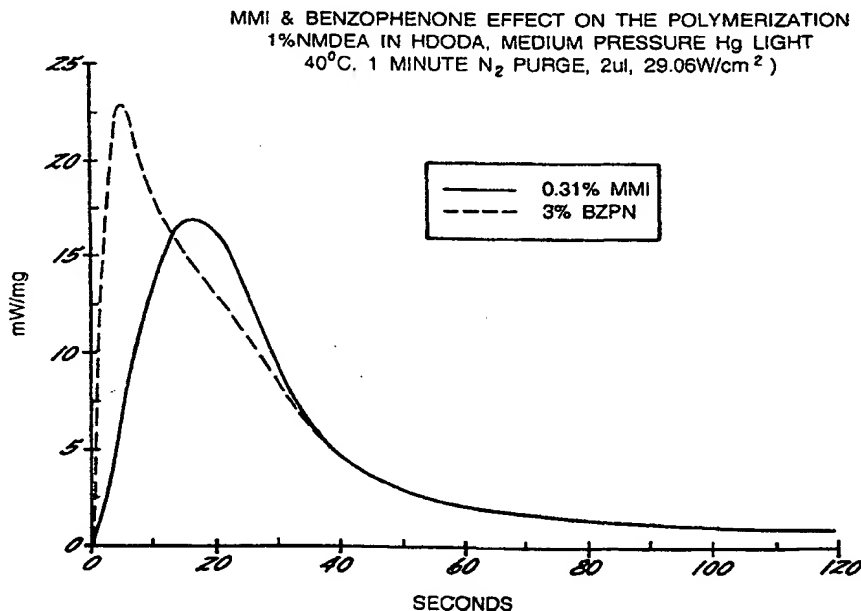
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(54) Title: PHOTOPOLYMERIZATION COMPOSITIONS INCLUDING MALEIMIDES AND PROCESSES FOR USING THE SAME



(57) Abstract

Photopolymerization compositions which include maleimides and processes using the same are disclosed. Polymerization of compositions which include maleimides in combination with a benzophenone compound/hydrogen atom donor sensitizer system may be activated by irradiating the compositions with radiation.

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PHOTOPOLYMERIZATION COMPOSITIONS INCLUDING MALEIMIDES AND PROCESSES FOR USING THE SAME

Field of the Invention

This invention relates generally to photopolymerizable compositions and more particularly to photopolymerizable compositions which include maleimide
5 compounds as a component and methods of using the same.

Background of the Invention

Ethylenically unsaturated compounds, such as acrylate derivatives, can be polymerized by exposure to radiation, typically ultraviolet light, in the presence of
10 a photoinitiating system. Typically, the photoinitiating system includes (1) a compound capable of initiating polymerization of the ethylenically unsaturated compound upon exposure to radiation (a "photoinitiator") and optionally (2) a coinitiator or synergist, that is, a molecule which serves as a hydrogen atom donor. The coinitiators or synergists are typically alcohols, tertiary amines, amides, or ethers
15 which have labile hydrogens attached to a carbon adjacent to a heteroatom. Currently commercially available photoinitiators include benzophenones and derivatives thereof, such as thioxanthone derivatives.

Maleimides, and in particular N-aliphatic and ortho-substituted (i.e. "twisted") N-aromatic maleimides have been investigated as comonomer-
20 photoinitiators of UV-curable acrylic systems. These maleimides have been observed to require the presence of a hydrogen atom-donor synergist (such as an amine, ether, thiol, or the like) to obtain reasonable rates of initiation and polymerization.

J. Put and F.C. De Schryver, "Photochemistry of Nonconjugated Bichromophoric Systems," Journal of the American Chemical Society. 95, 1, 137-45
25 (1973); "Photocycloaddition Polymerization. I. Preparation and Characterization of Poly-N,N'-polymethylenebis(dichloromaleimides)," Journal of Polymer Science: Part A-1. 8, 1939-48 (1970); and N. Boens et al., "Solid-State Ultraviolet Irradiation of Some Maleimides and Bismaleimides," Journal of Polymer Science: Polymer
Chemistry Edition 13, 210-13 (1975) report studies of the sensitization of maleimides
30 with benzophenone and thioxanthenes for the formation of maleimide 2 + 2 cycloadducts. F.C. De Schryver, et al, "Photochemistry of Nonconjugated

Bichromophoric Systems. Photopolymerization of N,N-Alkylenebis (dimethylmaleimides)," Journal of the American Chemical Society 96, 20, 6463-69 (1974) also report the formation polymer networks by the sensitized step-wise 2 + 2 cycloaddition of maleimides.

5

Summary of the Invention

The present invention is directed to photopolymerizable compositions and methods for radiation curing of the same. The compositions of the invention include at least one radiation curable compound. The compositions preferably include
10 ethylenically unsaturated compounds, and in particular, acrylate derivatives.

The compositions further include at least one maleimide which is capable of initiating the photopolymerization of a radiation curable compound. The maleimide can be an alkyl maleimide, functionalized aliphatic maleimide, aromatic maleimide, maleimide, maleic anhydride, or mixtures thereof. The maleimide
15 component can be substantially completely consumed during initiation and photopolymerization (incorporated into the polymer structure).

The composition further includes additional photoactive compounds as sensitizers. Specifically, the composition includes at least one benzophenone compound which is capable of initiating polymerization of the ethylenically
20 unsaturated compound upon exposure to radiation. As used herein, the term "benzophenone compound" includes benzophenone and derivatives thereof, including thioxanthone and derivatives of thioxanthone. In addition, the composition optionally includes at least one coinitiator or synergist as a hydrogen atom donor or an electron donor. The hydrogen atom donor can be present as a separate compound or can be
25 included as a molecular component of the photopolymerizable compound. The synergistic effect described herein which occurs when a sensitizer is used in conjunction with a maleimide in the presence of a hydrogen atom donor has been observed to dramatically increase rates of polymerization of typical acrylic photo-curable systems, as compared to rates obtained using the same acrylic photo-curable
30 system with either maleimide with a hydrogen-atom donor or the sensitizer with a hydrogen-atom donor as the initiating system.

The present invention also provides methods for radiation curing of photopolymerizable compositions of the invention.

Brief Description of the Drawings

Some of the features and advantages of the invention having been described, others will become apparent from the detailed description which follows,
5 and from the accompanying drawings, in which:

Figure 1 is a graph illustrating photo-differential scanning calorimetry (DSC) exotherm rates for the photopolymerization of 1,6-hexanediol diacrylate (HDDA) with photoinitiator packages of 3% benzophenone (BZPN)/1% methyl diethanol amine (NMDEA) and 0.31% N-methyl maleimide (MMI)/1% NMDEA;

10 Figure 2 is a graph illustrating photo-DSC exotherm rates for the photopolymerization of polyethylene glycol diacrylate (PEG 400 DA) with photoinitiator packages of 3% BZPN/1% NMDEA and 0.31% MMI/1% NMDEA;

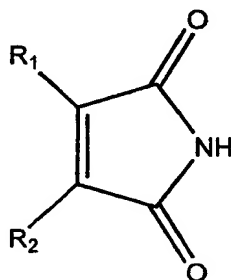
Figure 3 is a graph illustrating photo-DSC exotherm rates for the photopolymerization of HDDA with photoinitiator packages of 3% BZPN/1% NMDEA, 0.31% MMI/1% NMDEA, and 3% BZPN/0.31% MMI/1% NMDEA;

15 Figure 4 is a graph illustrating photo-DSC exotherm rates for the photopolymerization of HDDA with photoinitiator packages of 3% BZPN/0.31% n-phenyl maleimide (N-PHMI)/1% NMDEA, 3% BZPN/0.31% N-hexyl maleimide (N-HMI)/1% NMDEA, 3% BZPN/0.31% N-cyclohexyl maleimide (N-CHMI)/1% NMDEA, 3% BZPN/0.31% maleic anhydride/1% NMDEA, and 3% BZPN/3% Irgacure 651 (α,α -dimethoxy deoxybenzoin (BDK)); and

25 Figure 5 is a graph illustrating photo-DSC exotherm rates for the photopolymerization of HDDA with photoinitiator packages of 3% BZPN/0.31% maleimide (MI)/1% NMDEA, 3% BZPN/0.31% N-2-n-tert-butyl-phenyl maleimide/1% NMDEA, 3% BZPN/0.31% DEFMR (diethylfumarate)/1% NMDEA, 3% BZPN/0.31% HMI/1% NMDEA, and 3% BZPN/0.31% maleic anhydride/1% NMDEA.

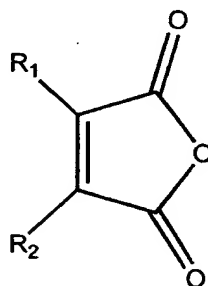
Detailed Description of the Invention

Maleimides useful in the compositions of the invention include maleimides of the formula



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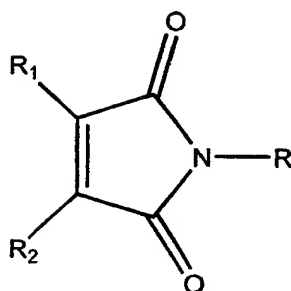
and maleic anhydrides of the formula



wherein:

each R₁ and R₂ is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R₁ and R₂ together form a fused saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system containing one or two O, N or S atoms, optionally substituted with alkyl, aryl, halogen, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like. Such compounds are commercially available and/or can be prepared using commercially available starting materials using techniques known in the art.

Alkyl maleimides useful in the invention include compounds having at least one maleimide functional group substituted with a linear, branched or cyclic C1-C10 alkyl radical at the nitrogen atom. Exemplary alkyl maleimide compounds can have the formula below:



wherein:

each R₁ and R₂ is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R₁ and R₂ together form a fused saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system containing one or two O, N or S atoms, optionally substituted with alkyl, aryl, halogen, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like; and

R is straight chain, branched or cyclic C1-C10 alkyl, optionally substituted with one or more C1-C4 alkyl, and preferably is C1-C4 alkyl or C6 cycloalkyl.

Exemplary alkyl maleimides include without limitation methyl maleimide, hexyl maleimide, cyclohexyl maleimide, and the like. Such compounds are known in the art and can be prepared using techniques known in the art. See, for example, Z.Y. Wang, Synthetic Comm. 20(11) 1607-1610 (1990); P.O. Tawney et al., J. Org. Chem. 26, 15 (1961); and U.S. Patent No. 2,542,145.

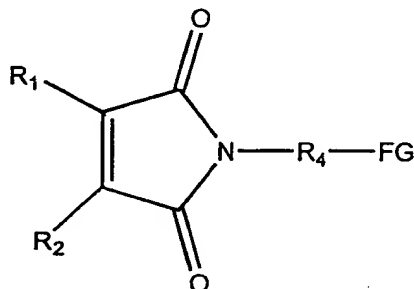
Aliphatic maleimide compounds useful in the invention include compounds having at least one maleimide unit substituted with a functionalized aliphatic substituent at the nitrogen atom. The aliphatic substituent preferably is a linear or branched C1 to C10 alkyl, and more preferably methyl or ethyl. The alkyl is optionally substituted with C1 to C4 alkyl, C1 to C4 alkoxy, halogen, and the like as described below.

Aliphatic maleimides useful in the invention can be monofunctional (have one maleimide functional group), or can be di- or multi-functional (have two or more maleimide functional groups). For example, two or more aliphatic maleimide units can be connected or coupled via a spacer group(s), such as, but not limited to, linear or branched C1 to C10 alkyl, C3 to C6 cycloalkyl optionally substituted with C1 to C4 alkyl, C1 to C10 oxyalkyl, which can include one or more oxygen atoms,

such as that derived from ethylene glycol, carbonate, aryl, alkylaryl, arylalkyl, and the like. Still further, maleimide compounds useful in the invention include maleimide units connected to polymeric or oligomeric compounds (typically having a molecular weight of at least about 1000). For example, unsaturated polyester resins with

5 varying percent maleimide functionality incorporated therein as known in the art can be used.

Exemplary aliphatic maleimide compounds can have the formula below:



10 wherein:

(a) each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system containing one or two O, N or S atoms,

15 optionally substituted with alkyl, aryl, halogen, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like;

(b) R_4 is linear or branched C1 to C10 alkyl, heteroatom, or silicon - SiH_2 -; and

(c1) when R_4 is C1 to C10 alkyl, FG is a functional group selected

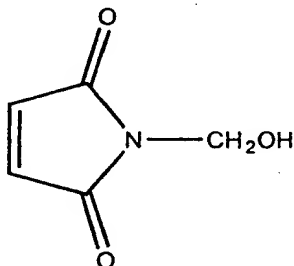
20 from the group consisting of $-\text{OR}_3$, $-\text{SR}_3$, $-\text{SiH}_2\text{R}_3$, $-\text{OC}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{C}(\text{=CHR}_3)\text{R}_3$, $-\text{OC}(\text{O})\text{R}_3$, $-\text{C}(\text{O})\text{R}_3$, $-\text{N}(\text{R}_3)_2$, $-\text{C}(\text{O})\text{OR}_3$, $-\text{NCO}$, $-\text{C}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{OR}_3$, $-\text{CN}$, halogen, $-\text{CH}_2\text{N-aryl-FG}'$, $-\text{CH}_2\text{N-aryl-R}_3\text{-FG}'$, sulfonic acid, quaternary ammonium, and salts thereof, in which each R_3 is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl, and in which

25 FG' is selected from the group consisting of $-\text{OR}_3$, $-\text{SR}_3$, $-\text{SiH}_2\text{R}_3$, $-\text{OC}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{C}(\text{=CHR}_3)\text{R}_3$, $-\text{OC}(\text{O})\text{R}_3$, $-\text{C}(\text{O})\text{R}_3$, $-\text{N}(\text{R}_3)_2$, $-\text{C}(\text{O})\text{OR}_3$, $-\text{NCO}$, $-\text{C}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{OR}_3$, $-\text{CN}$, halogen, sulfonic acid, and quaternary ammonium, or

(c2) when R₄ is a heteroatom or silicon -SiH₂-, FG is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, alkylaryl, arylalkyl, alkyl-FG", and aryl-FG", wherein FG" is the same as FG' as defined in (c1) above, or

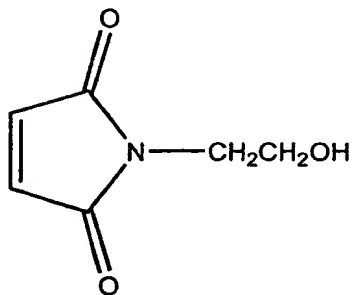
(c3) FG is a functional group as defined in (c1) in combination with a
5 spacer group linking said maleimide unit with at least one other maleimide unit to form a di- or multifunctional maleimide compound. Exemplary spacer groups include without limitation linear or branched C1 to C10 alkyl, C3 to C6 cycloalkyl, optionally substituted with lower C1 to C4 alkyl, C1 to C10 oxyalkyl, which can include one or more oxygen atoms, such as that derived from ethylene glycol, carbonate, and the
10 like. Aliphatic maleimides useful in the invention are described, for example, in pending U.S. application Serial No. 08/917,024, filed August 22, 1997, titled "Polymerization Processes Using Aliphatic Maleimides," and its corresponding published international application PCT Publication No. WO 98/07759, the entire disclosure of each of which is hereby incorporated by reference.

15 Exemplary aliphatic maleimides useful in the invention include, but are not limited to:
hydroxy methylmaleimide (HMMI)

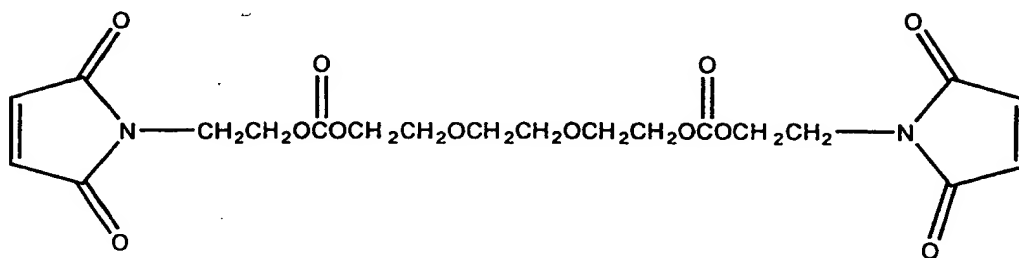


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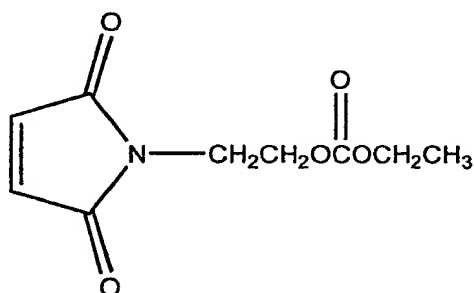
hydroxy ethylmaleimide (HEMI)



triethylene glycol biscarbonate bisethylmaleimide (TEGBCBEMI)

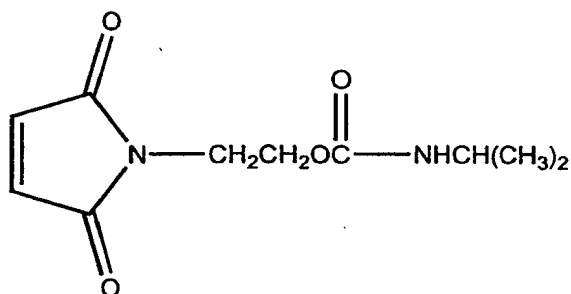


5 2-ethylcarbonate ethylmaleimide (2ECEMI)

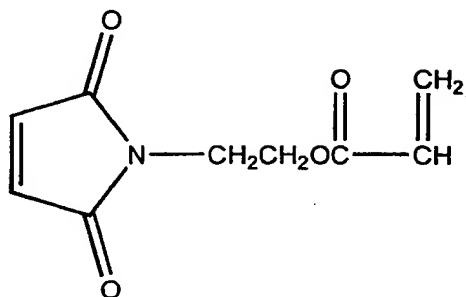


2-isopropyl urethane ethylmaleimide (2IPUEMI)

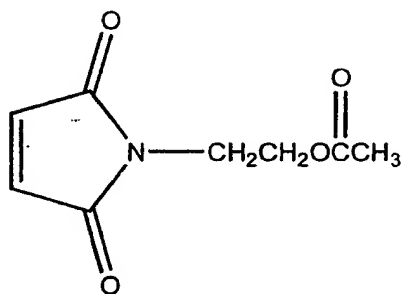
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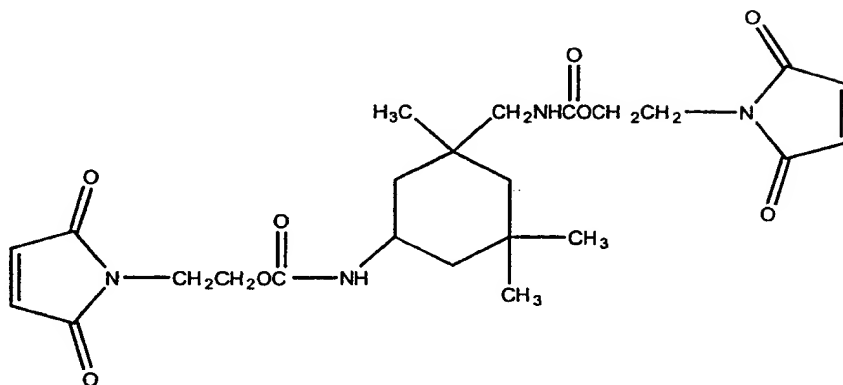
2-acryloyl ethylmaleimide (2AEMI)



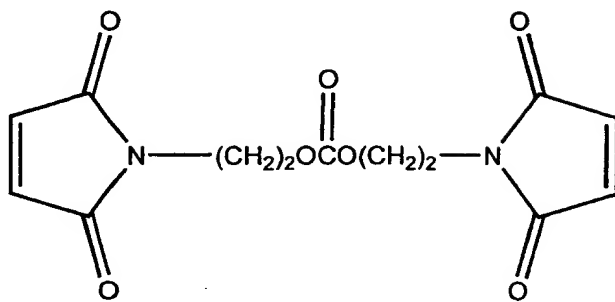
5 acetoxy ethyl maleimide (AcOEMI)



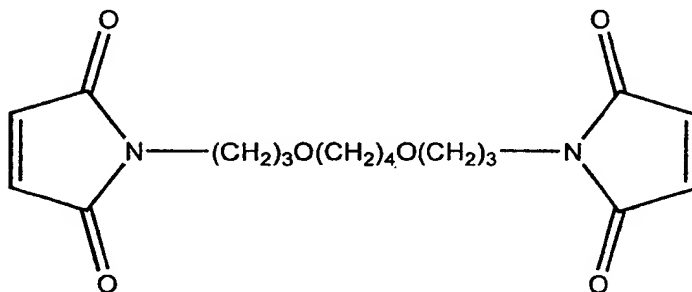
isophorone bisurethane bisethylmaleimide (IPBUBEMI)



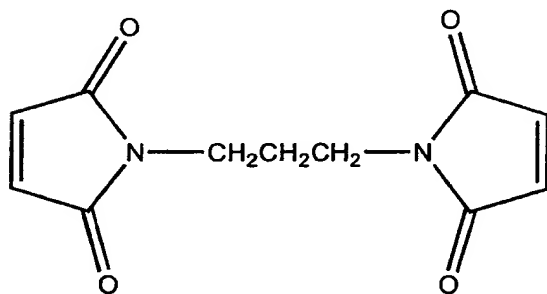
bisethylmaleimide carbonate (BEMIC)



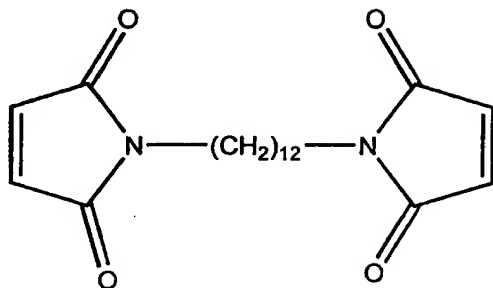
5 4,9-dioxa-1,12 dodecane bismaleimide (4,9-DO-1,12-DDBMI)



bispropyl maleimide (BPMI)



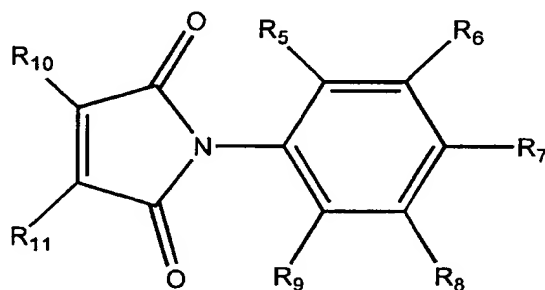
dodecane N,N'-bismaleimide



and the like.

Generally, aliphatic maleimides which include at least one maleimide
 5 unit as described above can be prepared using techniques known in the art. See, for
 example, Z.Y. Wang, Synthetic Comm. 20(11) 1607-1610 (1990); P.O. Tawney et al.,
 J. Org. Chem. 26, 15 (1961); and U.S. Patent No. 2,542,145.

Aromatic maleimides useful in invention include compounds
 according to formula below:



10

wherein:

each of R₅, R₆, R₇, R₈, and R₉ is independently selected from the group
 consisting of H, CX₃, COOR₁₂, COR₁₂, OR₁₂, CN, SR₁₂, N(R₁₂)₂, R₁₃, X, and MI;

R₁₀ and R₁₁ each is independently selected from the group consisting
 15 of H, C1 to C10 alkyl, preferably C1-C4 alkyl, more preferably CH₃, cycloalkyl, aryl,
 alkoxy, and halogen, preferably chloride, or R₁ and R₂ together form a fused saturated
 or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system
 containing one or two O, N or S atoms, optionally substituted with alkyl, aryl,
 halogen, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like;

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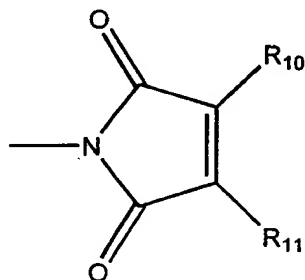
X is halide, preferably F, Cl, Br, or I;

R_{12} is selected from the group consisting of H, lower alkyl, cycloalkyl, and aryl;

R_{13} is selected from the group consisting of lower alkyl, cycloalkyl, and aryl, or R_{13} is a spacer group connecting at least two compounds of the above

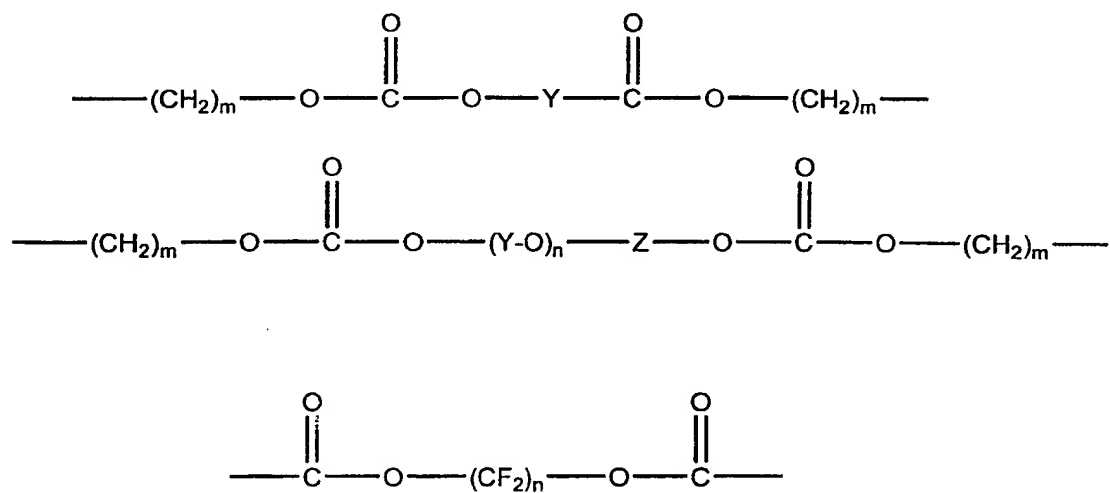
5 formula to form a di- or multi-functional maleimide; and

MI is



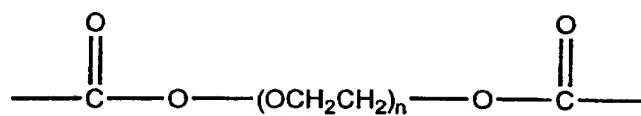
wherein R_{10} and R_{11} are as defined above. For example, two or more aromatic
10 maleimide units can be connected or coupled via a spacer group(s), such as, but not limited to, linear or branched C1 to C10 alkyl, C3 to C6 cycloalkyl optionally substituted with C1 to C4 alkyl, C1 to C10 oxyalkyl, which can include one or more oxygen atoms, such as that derived from ethylene glycol, carbonate, aryl, alkylaryl, arylalkyl, and the like. The spacer group can be, for example:

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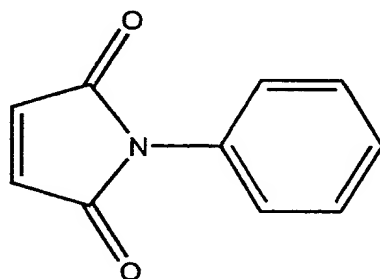
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and

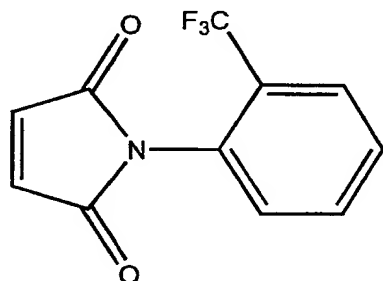


wherein Y and Z are each independently selected from C2 to C10 alkylene, m is an integer from 1 to 10, and n is an integer from 1 to 10;

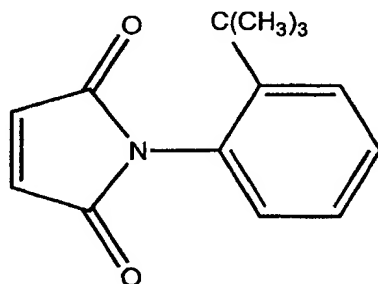
- Exemplary aromatic maleimides useful in the invention include, but
 5 are not limited to:
 phenyl maleimide (PMI)



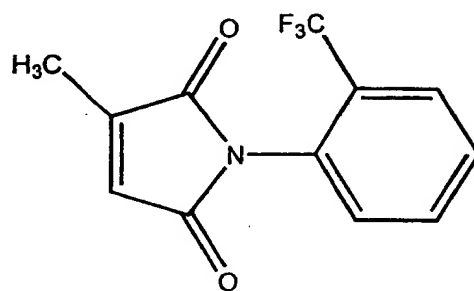
- N-(2-CF₃-phenyl)maleimide (2CF₃PMI)
 10



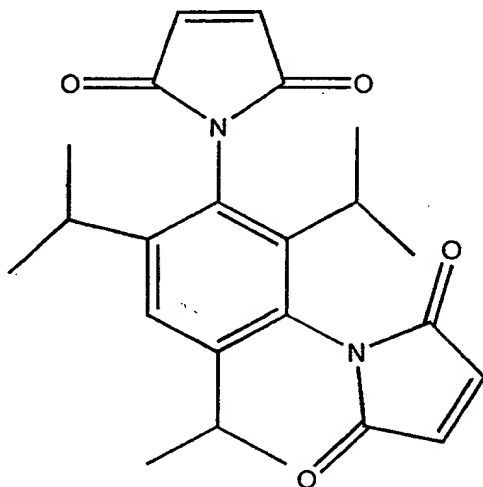
- N-(2-t-butylphenyl)maleimide (NtBPMI)



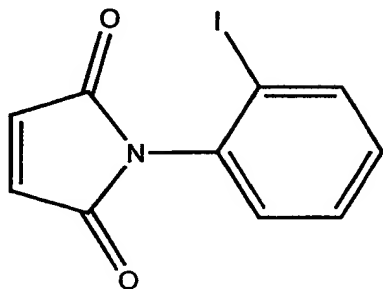
N-(2-CF₃-phenyl)methylmaleimide (2CF₃PCI)



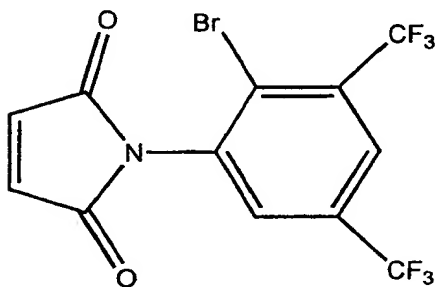
N-(2,4,6-isopropyl-3-maleimide phenyl)maleimide



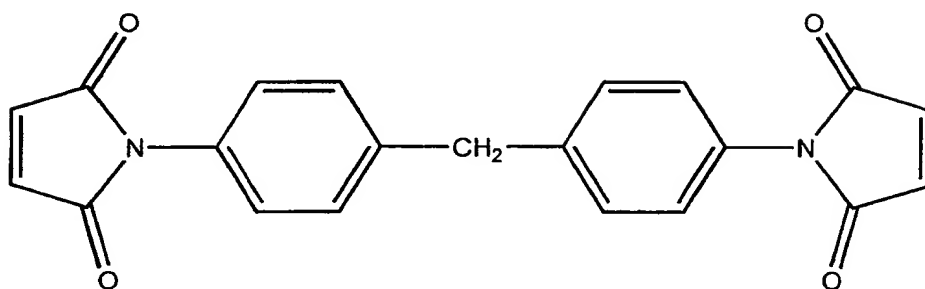
N-(2-iodophenyl) maleimide



5 N-(2-bromo-3,5-difluorophenyl) maleimide

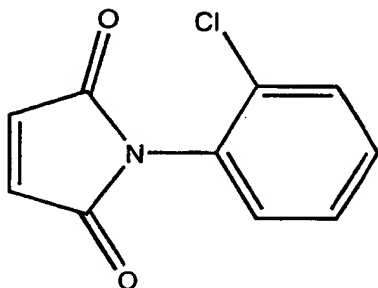


di(4-maleimidophenyl)methane



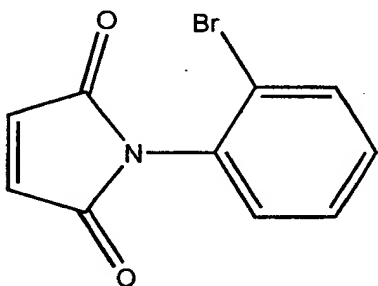
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N-(2-chlorophenyl) maleimide

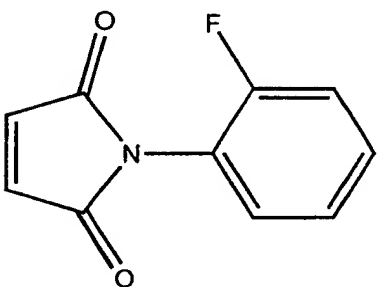


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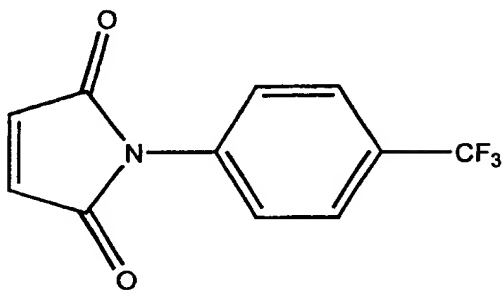
N-(2-bromophenyl) maleimide



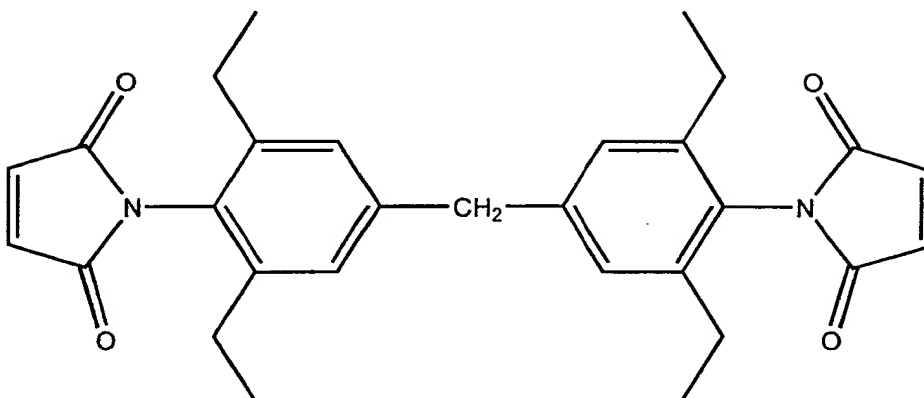
N-(2-fluorophenyl) maleimide



10

N-(4-CF₃-phenyl) maleimide

5 di(3, 5-diethyl-4-maleimidophenyl)methane



and the like.

Generally, aromatic maleimides can be prepared using techniques known in the art, with slight modifications as noted herein. The compounds, for example, can be synthesized using a two step method, which begins with the reaction of a suitably substituted aromatic amine with maleic anhydride (or a substituted maleic anhydride, such as citraconic anhydride) in a polar solvent, such as diethylether, to produce the amic acid in near quantitative yields. The amic acid is then recovered from the solvent and residual solvent and water can be removed from the recovered product.

The second step is acid catalyzed ring closure to form the imide. This reaction is performed by dissolving the amic acid in a suitable solvent, such as an organic hydrocarbon solvent such as toluene, optionally with a small amount of cosolvent, such as dimethylsulfoxide (DMSO), adding a catalytic amount of concentrated sulfuric acid, heating the mixture, preferably to reflux, and removing water through the water/solvent azeotrope. Excess solvent can then be removed, and

the residual concentrated solution of the imide in solvent precipitated. The imide is then collected and dried to remove water and residual solvent(s). The second step can also give near quantitative yields. Aromatic maleimides useful in the invention are described, for example, in pending provisional application Serial No. 60/047,729, 5 filed May 27, 1997, titled "Aromatic Maleimides," and its corresponding published international application PCT Publication No. WO 98/54134, the entire disclosure of each of which is hereby incorporated by reference.

As used herein, the term alkyl refers to linear or branched C1 to C10 alkyl, such as but not limited to methyl, ethyl, propyl, butyl, isopropyl, and the like, 10 optionally substituted with halogen, aryl, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like. The term alkoxy refers to linear or branched C1 to C10 alkoxy. The term cycloalkyl refers to C3 to C6 cycloalkyl, such as but not limited to cyclopentyl and cyclohexyl, also optionally substituted with halogen, aryl, alkyl, arylalkyl, alkylaryl, alkoxy, heteroatoms, silicon and the like. The term aryl 15 refers to C3 to C10 cyclic aromatic groups such as but not limited to phenyl, naphthyl, and the like, optionally substituted with halogen, alkyl, arylalkyl, alkylaryl, cycloalkyl, alkoxy, heteroatoms, silicon, and the like. The term heteroatom refers to oxygen, sulfur, and nitrogen.

The photopolymerizable compositions include at least one maleimide 20 as defined above as a component thereof, for example, as a photoinitiator, a comonomer, and the like. As used herein, and as will be appreciated by the skilled artisan, the term photopolymerizable composition refers to compositions which harden or cure upon exposure to radiation.

Generally the compositions of the invention include ethylenically 25 unsaturated compounds, including monomers and oligomers derived from acrylic and methacrylic acid, optionally dispersed or dissolved in a suitable solvent that is copolymerizable therewith, and mixtures thereof, which are photopolymerizable when exposed to a source of radiation (ultraviolet or UV radiation, or radiation outside the UV spectrum), particularly free radical polymerizable systems. As will be 30 appreciated by the skilled artisan, the photopolymerizable compounds can be monofunctional, or can include two or more polymerizable ethylenically unsaturated groupings per molecule.

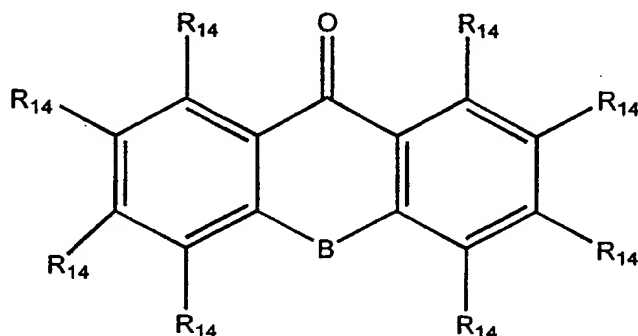
Exemplary photopolymerizable compounds or precursors include, but are not limited to, reactive vinyl monomers, including acrylic monomers, such as acrylic and methacrylic acids, and their amides, esters, salts and corresponding nitriles. Suitable vinyl monomers include, but are not limited to, methyl acrylate, ethyl acrylate, n- or tert-butylacrylate, isooctyl acrylate, methyl methacrylate, ethylmethacrylate, 2-ethylhexyl methacrylate, butylacrylate, isobutyl methacrylate, the corresponding hydroxy acrylates, i.e., hydroxy ethylacrylate, hydroxy propylacrylate, hydroxy ethylhexyl methacrylate, glycol acrylates, i.e., ethylene glycol dimethacrylate, hexamethylene glycol dimethacrylate, the allyl acrylates, i.e., allyl methacrylate, diallyl methacrylate, the epoxy acrylates, i.e., glycidyl methacrylate, and the aminoplast acrylates, i.e., melamine acrylate. Others such as vinyl acetate, vinyl and vinylidene halides and amides, i.e., methacrylamide, acrylamide, diacetone acrylamide, vinyl and vinylidene esters, vinyl and vinylidene ethers, vinyl and vinylidene ketones, butadiene, vinyl aromatics, i.e., styrene, alkyl styrenes, halostyrenes, alkoxy styrenes, divinyl benzenes, vinyl toluene, and the like are also included. Prepolymers include acrylated epoxides, polyesters and polyurethanes, and are typically combined with a suitable monomer for viscosity control.

The photopolymerizable compounds may be polymerized to form homopolymers or copolymerized with various other monomers.

The photopolymerizable compound can be present in the compositions of the invention in amounts from about 0 to about 99.8, preferably about 80 to about 99.8, percent by weight, based on the total weight of the composition.

The maleimides can be used singly or as mixtures thereof, and are useful as photopolymerization initiators. In this aspect of the invention, the maleimide compounds can be present in the photopolymerizable composition in an amount sufficient to initiate polymerization thereof upon exposure to radiation. The composition can include about 0.01 to about 100, preferably about 0.01 to about 20, more preferably about 0.01 to about 10, percent by weight maleimide compound, based on the total weight of the photopolymerizable compounds. The inventors have found that only relatively low concentrations of the maleimide are required for desirable results. For example, the maleimide can be present in amounts of about 0.01 mole percent to about 2 mole percent, and even less than about 0.1 mole percent.

The benzophenone compound can be benzophenone or any derivative thereof, including thioxanthone and derivatives thereof, and mixtures of such compounds, having photoactive activity. Such compounds are known in the art and include compounds of the following structure:



5

wherein:

B is (H,H), -CH₂-, -S-, -O-, -CO-, -NR₁₅-, or a bond bridging the two aromatic rings;

each R₁₄ is independently selected from the group consisting of
 10 hydrogen, alkyl, cycloalkyl, alkoxy, aryl, alkylaryl, arylalkyl, halogen, trihaloalkyl, -CN, -NO₂, -C(O)OR₁₅, -C(O)R₁₅, -OR₁₅, -N(R₁₅)₂, -OC(O)CR₁₅=CHR₁₅, R₁₆, -OR₁₆, -R₁₇-OC(O)CR₁₅=CHR₁₅, polymerizable moieties, and oligomeric and polymeric moieties;

R₁₅ is selected from the group consisting of hydrogen, alkyl, aryl,
 15 cycloalkyl, arylalkyl, and alkylaryl;

R₁₆ is one or more saturated or unsaturated five or six membered hydrocarbon or heterocyclic ring system, optionally substituted with one or more alkyl, cycloalkyl, or halogen; and

R₁₇ is selected from the group consisting of alkyl, aryl, cycloalkyl,
 20 arylalkyl, and alkylaryl.

The term polymerizable moiety refers to ethylenically unsaturated moieties known in the art which are capable of reaction with another compound (for example, by a free radical mechanism), such as but not limited to, acrylate and methacrylate moieties. For example, R₁₄ can have the structure -(CH₂)_n-OC(O)-
 25 CRH=CH₂ wherein n is an integer from 1 to 10 and R is H or lower alkyl. Another exemplary polymerizable entity is a maleimide moiety as described above.

The terms oligomeric and polymeric moieties refer to a moiety including two or more monomer units (dimer, trimer, etc.), typically having a molecular weight of at least about 500, and higher. Thus the benzophenone compound can be an oligomer or polymer having one or more benzophenone functionalities incorporated therein (along the backbone and/or side chain). Exemplary oligomeric and polymeric moieties include but are not limited to a C2-C20 alkylene or polyalkylene polyol, wherein hydroxy groups of the polyol moiety are optionally alkylated, and preferably an alkylene or polyalkylene polyol derived from ethylene glycol. Other suitable oligomer or polymer moieties include C2-C20 alkylene or polyalkylene moieties end capped with trihaloalkyl, and optionally substituted with one or more halogen atoms along the chain, preferably fluorine. Other exemplary oligomeric or polymer moieties include C2-C20 alkylene or polyalkylene moieties including carbonate groups and end capped with lower alkyl. Other exemplary oligomeric or polymeric moieties include polyether ketones and polyacrylate and polymethacrylate based compounds. Such oligomeric and polymeric benzophenones are known in the art and are commercially available.

Exemplary benzophenone compounds useful in the invention include without limitation benzophenone, thioxanthone, isopropylthioxanthone, chlorothioxanthone, methyl o-benzoylbenzoate, 4-morpholinobenzophenone, 4,4'-diphenoxybenzophenone, 1-methyl-2-(2-ethylhexyloxy)thioxanthone, 4,4'-di-(4-isopropylphenoxy)benzophenone, acrylic acid 4-benzoylphenyl ester, 4,4'-diphenylbenzophenone, 4-phenylbenzophenone, and the like, as well as mixtures thereof. These and other benzophenone compounds are known in the art and are commercially available or can be produced using commercially available starting materials. The benzophenone photoinitiator can be present in an amount ranging from about 0.001 to about 5 percent by weight, based on the total weight of the composition.

The sensitizer package also includes at least one coinitiator or synergist, that is, a molecule which serves as a hydrogen atom donor or an electron donor. Coinitiators or synergists are known in the art, and are typically alcohols, tertiary amines or ethers which have available hydrogens attached to a carbon adjacent to a heteroatom. The hydrogen atom donor can be present as a separate compound or can be included as a molecular component of the photopolymerizable

compound (for example, polyethylene glycol diacrylate). Such coinitiators when a separate component are typically present in an amount between about 0.1 and about 5 percent by weight based on the total weight of the composition. When present as a molecular component of a photopolymerizable compound, the hydrogen atom donor component can be up to about 85 weight percent, and higher, of the photopolymerizable compound. Suitable compounds include, but are not limited to, triethanolamine, methyl-diethanolamine, ethyldiethanolamine and esters of dimethylamino benzoic acid. Other known coinitiators or accelerators can also be used.

10 The photopolymerizable compositions of the invention may also contain other conventional agents, such as polymerization inhibitors, fillers, ultraviolet absorbers, organic peroxides, dyes, pigments, and the like.

 The photopolymerizable compositions can be applied or deposited on a surface of a substrate using conventional techniques and apparatus. The composition can be applied as a substantially continuous film. Alternatively, the composition can be applied in a discontinuous pattern. The thickness of the deposited composition can vary, depending upon the desired thickness of the resultant cured product.

 Typically, the substrate is coated with the uncured photopolymerizable composition and passed under a commercially available UV or excimer lamp on a conveyer moving at predetermined speeds. The substrate to be coated can be, for example, metal, wood, mineral, glass, paper, plastic, fabric, ceramic, and the like.

 The active energy beams used in accordance with the present invention may be visible light or ultraviolet light or may contain in their spectra both visible and ultraviolet light. The polymerization may be activated by irradiating the composition with ultraviolet light using any of the techniques known in the art for providing ultraviolet radiation, i.e., in the range of 200 nm and 450 nm ultraviolet radiation, and especially with the 308 nm emission from xenon chloride excimer lamps, commercially available from Fusion Systems, or by irradiating the composition with radiation outside of the ultraviolet spectrum. The radiation may be natural or artificial, monochromatic or polychromatic, incoherent or coherent and should be sufficiently intense to activate the photoinitiators of the invention and thus the polymerization. Conventional radiation sources include fluorescent lamps, excimer lamps, mercury, metal additive and arc lamps. Coherent light sources include pulsed nitrogen, xenon,

argon ion- and ionized neon lasers whose emissions fall within or overlap the ultraviolet or visible absorption bands of the compounds of the invention.

The compositions are useful in any of the types of applications known in the art for photopolymerizations, including as a binder for solids to yield a cured product in the nature of a paint, varnish, enamel, lacquer, stain or ink. The compositions can also be useful in the production of photopolymerizable surface coatings in printing processes, such as lithographic printing, screen printing, and the like. The compositions can also be useful in applications in which the compositions are applied to articles which are to be exposed to the environment, such as signage. Radiation cured coatings produced using conventional photoinitiators typically degrade over time (as evidenced by yellowing, increasing brittleness, and the like), which degradation is exacerbated by direct exposure to sunlight. In contrast, radiation cured coatings prepared using the maleimide compounds can exhibit minimal degradation over time, even when exposed to direct sunlight. The maleimides can also be water soluble.

The present invention will be further illustrated by the following non-limiting examples.

EXAMPLE 1

Synthesis of Hydroxy Methylmaleimide (HMMI)

Maleimide (10 g, 0.103 mol) was added to 10 mL of a 37% solution of formaldehyde and 0.31 mL of a 5% solution of NaOH was added. Within 10 minutes all of the maleimide had dissolved and an exothermic reaction proceeded. The solution was stirred for 2 hours where white crystals were observed. The solution was placed in a freezer overnight and the resulting crystals filtered and washed with ice cold ethanol and diethyl ether. The white crystals were purified twice by sublimation. See P. O. Tawney, R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams J. Org. Chem. 26, 15 (1961).m.p. 104-106°C (9.77 g, 74.6%). ¹H-NMR (Acetone-d₆, δ, ppm): 4.96 (2H, -CH₂-, s), 5.33 (1H, -OH, s), 6.93 (2H, -CH=CH-, s). ¹³C-NMR (Acetone-d₆, δ, ppm): 60.9 (1C, -CH₂-), 135.6 (2C, -CH=CH-), 173.1 (1C, -C=O).

EXAMPLE 2

Synthesis of Hydroxy Ethylmaleimide (HEMI)

Ethanolamine (80.96 g, 1.32 mol) was added to 500 mL of ethanol and cooled to 0°C using an ice bath. 3,6-Endoxo-1,2,3,6-tetrahydrophthalic anhydride (220.21 g, 1.32 mol) was added to the solution and allowed to stir overnight. The yellow tinted crystals were used without purification. The solution was refluxed for four hours with azeotropic removal of water. The solution was cooled to 0°C and the resulting crystals filtered (151.74 g, 54.95 %). Removal of furan was facilitated by refluxing the crystals in xylenes for 4 hours with quantitative yield of hydroxy ethylmaleimide after purification by sublimation to yield white crystals, -CH₂O-, 134.2 (2C, -CH=CH-), 171.2 (2C, -NC=O m.p. 68°C. ¹H-NMR (CDCl₃, δ, ppm): 2.62 (1H, -OH, s), 3.82-3.77 (4H, -NCH₂CH₂O-, overlapping), 6.76 (2H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 40.5 (1C, -NCH₂-), 60.5 (1C,).

EXAMPLE 3

Triethylene Glycol Biscarbonate Bisethylmaleimide

(TEGBCBEMI)

HEMI (25.65 g, 0.182 moles) and pyridine (14.38 g, 0.182 moles) were dissolved in THF (130 mL) and the solution was stirred at room temperature. Triethylene glycol bischloroformate (25.0 g, 0.091 moles) was added dropwise and stirred for 90 minutes. The pyridine salt was filtered off and the solution was combined with 200 mL of a 1N HCl solution. The product was extracted with methylene chloride and washed with a 1N HCl solution followed by water and then dried over magnesium sulfate. The red solution was diluted to a volume of 150 mL and purified by column chromatography (2.5 cm x 21 cm) using silica gel as the packing and methylene chloride as the mobile phase yielding white crystals, m.p. 65°C (26.75 g, 60.76%). ¹H-NMR (CDCl₃, δ, ppm): 3.64-3.68 (4H φ-OCH₂-, t), 3.69-3.74 (4H, ε-OCH₂-, t), 3.81-3.86 (4H, -NCH₂-, t), 4.26-4.3 (8H, -CH₂O(C=O)OCH₂-, t), 6.75 (4H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 36.6 (2C, -NCH₂-), 64.7 (2C), 67.3 (2C), 68.8 (2C), 70.6 (2C), 134.4 (4C, -CH=CH-), 154.8 (2C, O(C=O)O), 170.4 (4C, -NC=O).

EXAMPLE 4

Synthesis of 2-Ethylcarbonate Ethylmaleimide (2ECEMI)

Hydroxy ethylmaleimide (29.87 g, 0.212 moles) and pyridine (16.7 g, 0.212 moles) were dissolved in THF (170 mL) and the solution was stirred at room temperature. Ethyl chloroformate (22.97 g, 0.212 moles) was added dropwise and stirred for 90 minutes. The pyridine salt was filtered off and the solution was combined with 200 mL of a 1N HCl solution. The product was extracted with methylene chloride and washed with a 1N HCl solution followed by water and then dried over magnesium sulfate. The red solution was concentrated and the red crystals purified by sublimation yielding white crystals, m.p. 52°C (34.76 g, 77.04%). ¹H-NMR (CDCl₃, δ, ppm): 1.26-1.34 (3H, -CH₃, t), 3.81-3.87 (2H -NCH₂-, t), 4.14-4.25 (2H, δ-CH₂OC=O, q), 4.25-4.30 (2H, β-CH₂O-, t), 6.74 (2H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 14.2 (1C, -CH₃), 36.8 (1C, -NCH₂-), 64.3 (1C, δ-CH₂O), 64.5 (1C, β-CH₂-), 134.4 (2C, -CH=CH-), 154.9 (1C, O(C=O)O), 170.4 (2C, -C=O).

EXAMPLE 5

Synthesis of 2-Isopropyl Urethane Ethylmaleimide (2IPUEM)

Hydroxy ethylmaleimide (5 g, 35.4 mmol) was dissolved in 75 mL of methylene chloride 1 drop of dibutyl tin dilaurate catalyst was added. Isopropyl isocyanate (3.01 g, 35.4 mmol) was added dropwise and the solution was stirred for 3 hours. The solution was washed with water dried with magnesium sulfate. Concentration yielded white crystals which were further purified sublimation yielding white crystals, m.p. 117°C (6.49 g, 81%). ¹H-NMR (CDCl₃, δ, ppm): 1.11-1.14 (6H, -C(CH₃)₂, d), 3.74-3.79 (2H, -NCH₂-, t), 4.28-4.32 (2H, -CH₂O-, t), 4.44-4.53 (1H, -CH-, p), 6.72 (2H, -OC-CH=CH-CO-, s). NMR ¹³C-NMR (CDCl₃, δ, ppm): 170.5 (2C, C=O, maleimide), 155.1 (1C, C=O, urethane), 134.2 (2C, -CH=CH-), 61.7 (1C, β-CH₂), 43.6 (1C, -CH-), 37.4 (1C, α-CH₂), 22.9 (2C, -CH₃).

EXAMPLE 6

Synthesis of 2-Acryloyl Ethylmaleimide (2AEMI)

2-Hydroxyethyl maleimide (5 g, 35.4 mmol) and Et₃N (4.25g, 43.0 mmol) was dissolved in 75 mL of methylene chloride and cooled to 0°C. Acryloyl chloride

(3.20 g, 35.4 mmol) in 25 mL of methylene chloride was added dropwise over 30 minutes. The solution was stirred at room temperature for 30 minutes followed by refluxing for 1 hour. The triethylamine hydrochloride was removed by filtration and the yellow solution was concentrated. The yellow crystals were purified by
5 sublimation yielding white crystals, m.p. 77-78°C (5.00 g, 72.3%). ¹H-NMR (CDCl₃, δ, ppm): 3.81-3.87 (2H, -NCH₂-, t) 4.22-4.33 (2H, -OCH₂-, t), 5.81-5.85 (2H, CH₂=CH, cis), 6.00-6.13 (1H, CH₂=CH-, q), 6.34-6.42 (1H CH₂=CH, trans), 6.73 (2H, -OC-CH=CH-CO-, s). ¹³C-NMR (CDCl₃, δ, ppm): 170.4 (2C, C=O, maleimide), 165.8 (1C, C=O, ester), 134.2 (2C, -CH=CH-), 131.45 (1C, -CH=), 127.9 (1C, CH₂=),
10 61.5 (1C, β-CH₂-), 36.8 (1C, α-CH₂-).

EXAMPLE 7

Synthesis of Acetoxy Ethyl Maleimide (AcOEMI)

Maleic anhydride (172.32 g, 1.75 mol) was added to ethanolamine
15 (107.34 g, 1.75 mol) and dissolved in 500 mL of acetone while stirring overnight in an ice bath. To the solution, 400 mL of acetic anhydride (4.23 mol) was added with sodium acetate (144 g, 1.75 mol). The solution was heated to 80°C and stirred for 1 hour. The contents were poured into ice water and the acetic acid neutralized with K₂CO₃. The product was extracted with methylene chloride and then dried using
20 magnesium sulfate. The product was purified by sublimation yielding white crystals, m.p. 76°C (44.1 g, 13.45%). ¹H-NMR (CDCl₃, δ, ppm): 2.02 (3H, -CH₃, s), 3.82-3.77 (2H, -NCH₂-, t), 4.25-4.20 (2H, -CH₂O-, t), 6.75 (2H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 20.7 (1C, -CH₃), 37.0 (1C, -NCH₂-), 61.5 (1C, -CH₂O-), 134.3 (2C, -CH=CH-), 170.5 (2C, -NC=O), 170.8 (1C, -OC=O).

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EXAMPLE 8

Synthesis of 4,9-Dioxa-1,12

Dodecane Bismaleimide (4,9-DO-1,12-DDBMI)

4,9-Dioxa-1,12-dodecane diamine (25 g, 0.122 mol) was dissolved in
30 acetone and added dropwise to a solution of maleic anhydride (24 g 0.244 mol) in 120 mL of acetone under cooling using an ice bath in a nitrogen atmosphere. The solution was stirred overnight and the contents were then poured into water and the bismaleamic acid filtered and washed with ethanol and diethylether.

The bismaleamic acid (29.96 g, 74.8 mmol) was dissolved in an acetone 120 mL and triethylamine (41.7 mL, 0.300 mol) solution. The solution was heated to reflux, where acetic anhydride (21.2 mL, 0.224 mol) was added dropwise, the solution was refluxed for 12 hours. The solution was added to ice water and the precipitate filtered and dried. The sample was purified by column chromatography using silica gel as the adsorbent and methylene chloride as the mobile phase yielding white crystals, m.p. 65°C (5.5 g, 20.2 %). ¹H-NMR (CDCl₃, δ, ppm): 1.60-1.54 (2H, ε-CH₂-), 1.91-1.78 (2H, β-CH₂-), 3.44-3.28 (4H, -CH₂OCH₂-), 3.66-3.59 (2H, -NCH₂-, t), 6.70 (2H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 26.4 (2C, ε-CH₂-), 28.6 (2C, β-CH₂-), 35.6 (2C, -NCH₂-), 68.2, 70.7 (4C, -CH₂OCH₂-), 134.2 (2C, -CH=CH-), 170.8 (2C, -NC=O).

EXAMPLE 9

Synthesis of Isophorone bisurethane bisethylmaleimide (IPBUBEMI)

Hydroxy ethylmaleimide (10 g, 0.141 mol) was dissolved in acetone and purged with nitrogen while stirring in an ice bath. One drop of dibutyl tin dilaurate was added to the solution. The isophorone diisocyanate (30.5 g, 0.141 mol) was added dropwise over 2-3 hours. The solution was allowed to stir overnight and a white precipitate was obtained after solvent removal m.p. 105-112°C (40.5 g, 100%). ¹H-NMR (D₆-DMSO, δ, ppm): 3.63-3.58 (2H, -NCH₂-), 4.08-4.03 (2H, -CH₂O-, t), 7.03 (2H, -CH=CH-, s). ¹³C-NMR (D₆-DMSO, δ, ppm): 134.5 (2C, -CH=CH-), 154.9 (2C, NHC=O), (170.7 (2C, -NC=O).

EXAMPLE 10

Synthesis of Bispropyl Maleimide (PBMI)

Diaminopropane was dissolved in 100 mL of dimethyl acetamide (DMAC) and added dropwise to a solution of maleic anhydride in DMAC under cooling using an ice bath in a nitrogen atmosphere. The solution was stirred overnight and the contents were then poured into water and the bismaleamic acid filtered and washed with ethanol and diethylether.

The bismaleamic acid (84.54 g, 0.312 mol) was dissolved in 312 mL of an acetone and triethylamine (87 mL, 0.624 mol) solution. The solution was heated to reflux and acetic anhydride (88 mL, 0.61 mol) was added dropwise through a reflux condenser and the solution was refluxed for 12 hours. The solution was added to ice

water and the precipitate filtered and dried. The sample was purified by column chromatography using silica gel as the adsorbent and methylene chloride as the mobile phase yielding white crystals, m.p. 166°C (19.28 g, 26.3%). ¹H-NMR (CDCl₃, δ, ppm): 2.00-1.86 (2H, -CH₂-, p), 3.57-3.50 (4H, -NCH₂-, t), 6.71 (2H, -CH=CH-, s).
5 ¹³C-NMR (CDCl₃, δ, ppm): 27.3 (1C, -CH₂-), 35.3 (2C, -NCH₂-), 134.2 (2C, -CH=CH-), 170.6 (2C, -NC=O).

EXAMPLE 11

Synthesis of Bisethylmaleimide Carbonate (BEMIC)

10 Hydroxy ethylmaleimide (10.0 g, 70.1 mmol) was dissolved in a solution of methylene chloride (71 mL) and triethylamine (9.87 mL, 70.8 mmol) and cooled with an ice bath to 0°C. Triphosgene (3.504 g, 12 mmol) was added over a period of 4 hours and the resulting solution filtered. The supernatant was washed with 1N hydrochloric acid, 5% potassium carbonate solution and water. The solution was
15 dried over magnesium sulfate and purified using activated carbon to yield white crystals (4.0 g, 18.5%). ¹H-NMR (CDCl₃, δ, ppm): 3.82 (4H, -NCH₂-, t), 4.27 (2H, -CH₂O-, t), 6.73 (2H, -CH=CH-, s). ¹³C-NMR (CDCl₃, δ, ppm): 36.6 (2C, -NCH₂-), 64.9 (2C, -CH₂O-), 134.2 (2C, -CH=CH-), 154.5 (1C, C=O) 170.8 (2C, -NC=O).

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EXAMPLE 12

Synthesis of N-(2-CF₃-phenyl)maleimide

32.5 g of maleic anhydride is placed in 700 mL diethylether and allowed to dissolve. 41.48 mL of 2-trifluoromethyl aniline is added squirtwise to the stirring solution. The reaction is allowed to proceed at room temperature overnight
25 and a pale white precipitate is observed. The stirring solution is then warmed for several hours and filtered, yielding a pale white solid. The mother liquor is then combined with the wash liquor and allowed to stir again, and additional product is filtered off. The solids are then combined and dried in vacuum. Typical yields are 90-98%.

30

44.8 g of the maleamic acid is then placed in a three necked flask with 100 mL toluene and 25 mL DMSO, and allowed to dissolve. 1.8 mL of concentrated sulfuric acid is then added to the stirring mixture, which is then heated to about 130° C. The reaction mixture is allowed to reflux for 4 hours or until an azeotrope is no

longer observed. Excess toluene is then removed via vacuum distillation. The mixture is then added to stirring distilled water to precipitate the imide and remove excess DMSO. The aqueous suspension is allowed to stir overnight and is then filtered. The pale white solid is then dried under vacuum to remove water, DMSO and toluene. Yields are typically 90-97%.

Products from both steps are analyzed using ^1H and ^{13}C NMR in d_6 -DMSO. The maleamic acid is characterized by a broad peak due to the acid proton near 13-14 ppm, a peak due to the amide proton near 10 ppm, and two doublets due to the ene protons near 6.4 ppm in the proton spectra. The maleamic acid is also characterized by two peaks near 165 ppm due to the two carbonyls in the carbon spectrum. The maleimide is characterized by the absence of the acid and amide proton peaks, and the single ene proton peak shifted to near 7.6 ppm in the proton spectrum. In the carbon spectrum the maleimide shows a single carbonyl peak near 170 ppm.

The melting point of N-(2- CF_3 -phenyl)maleimide is measured using DSC at a heating rate of $20^\circ\text{C}/\text{min}$ and found to be 115.91°C (endotherm peak maximum). Heat of fusion is also calculated to be 71.62 J/g .

EXAMPLE 13

Synthesis of N-(2-t-butylphenyl)maleimide

N-(2-t-butylphenyl)maleimide is also prepared as described in Example 12, except substituting 2-trifluoromethyl aniline with 2-tert-butyl aniline. The melting point of N-(2-t-butylphenyl)maleimide is measured using DSC at a heating rate of $20^\circ\text{C}/\text{min}$ and is found to be 99.64°C (endotherm peak maxima). Heat of fusion is also calculated to be 94.02 J/g .

EXAMPLE 14

Synthesis of N-(2- CF_3 -phenyl)methylmaleimide

N-(2- CF_3 -phenyl)methylmaleimide is also prepared as described in Example 12, except substituting citraconic anhydride for maleic anhydride.

EXAMPLE 15

Synthesis of N-(2-iodo-phenyl)maleimide

N-(2-iodo-phenyl)maleimide is prepared as described in Example 12, except substituting 2-trifluoromethyl aniline with 2-iodoaniline.

5

EXAMPLE 16

Synthesis of N-(2-bromo-3,5-CF₃-phenyl)maleimide

N-(2-bromo-3,5-CF₃-phenyl)maleimide is prepared as described in Example 12, except substituting 2-trifluoromethyl aniline with 2-bromo-3,5-trifluoromethyl aniline.

10

EXAMPLE 17

Photopolymerization Using

Benzophenone/Amine/Maleimide Formulation

Figure 1 is a graph illustrating photo-DSC exotherm rate results for the photopolymerization of a typical UV curable monomer (HDDA is 1,6-hexanediol diacrylate) with photoinitiator packages of benzophenone (BZPN)/1% methyl diethanol amine (NMDEA) and N-methyl maleimide (MMI)/1% NMDEA. For the results in Figure 1, the concentrations were adjusted to give comparable initiator absorbances. The benzophenone/NMDEA system generates a higher exotherm peak rate and a shorter time is required to attain the peak maximum as compared to the MMI/NMDEA system.

Similar results are illustrated in Figure 2 for the photopolymerization of polyethylene glycol (400) diacrylate (PEG 400 DA) which has abstractable hydrogens between the acrylate functionalities. While it is possible to achieve somewhat faster rates by using maleimides with groups that have abstractable hydrogens (such as heteroatom containing groups), the rates achieved are still quite small compared to conventional photoinitiator systems.

Figure 3 gives photo-DSC exotherm results in nitrogen saturated systems that incorporate three components (benzophenone sensitizer, methyl maleimide, and NMDEA) as the photoinitiator package for the polymerization of HDDA. The exotherm rate maximum increased dramatically when both methyl maleimide and benzophenone are present as compared to the exotherm rates for

30

systems in which methyl maleimide/NMDEA are present or in which benzophenone/NMDEA are used and maleimide has been excluded. In other words, the synergistic effect on polymerization rate of having the N-alkyl maleimide present is dramatic, resulting in a substantially faster overall curing process under the conditions employed. The results in Figure 3 were attained for systems in which the samples were exposed to the unfiltered 30 mW output of a medium pressure mercury lamp similar in spectral output (but lower in overall intensity) to the lamps used in the UV curing industry.

To extend the results shown in Figure 3, exotherms were recorded for the photopolymerization of HDDA initiated by exposing benzophenone/N-alkyl maleimide/NMDEA and benzophenone/N-aryl maleimide/NMDEA systems to the output of a filtered (365-nm mercury line filter) source (Figures 4 and 5). When either an N-alkyl or an N-aryl maleimide was used in combination with the benzophenone sensitizer, a dramatic increase in the polymerization rate was observed as compared to results using the benzophenone/NMDEA system alone. Results for maleic anhydride (Figures 4 and 5) and Irgacure-651 (BDK) (Figure 4) are shown for comparison. Figures 4 and 5 indicate that N-alkyl maleimides of widely varying structures (methyl maleimide MMI, hexyl maleimide HMI, and cyclohexyl maleimide CHMI) as well as both ortho-substituted (i.e., twisted) (tert-butyl maleimide NtBMI) N-aryl maleimides and simple substituted or unsubstituted (i.e., planar) (phenyl maleimide N-PMI) N-aryl maleimides (heretofore found to be ineffective upon direct excitation), can be sensitized to have much greater initiation efficiencies than benzophenone/NMDEA systems.

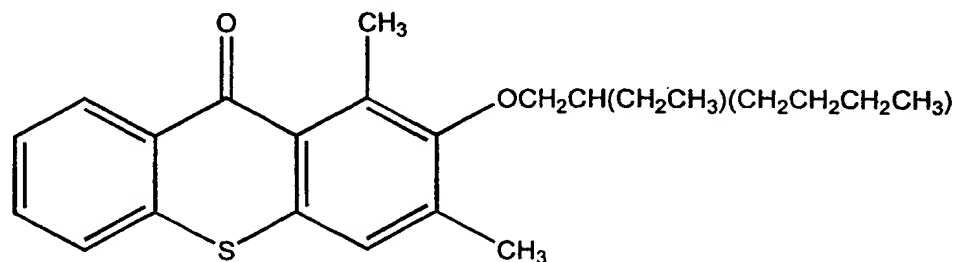
Although not wishing to be bound by any explanation of the invention, it is currently believed that energy transfer occurs from the excited state triplet of the benzophenone to the maleimide, which then abstracts a hydrogen atom and initiates the polymerization process.

EXAMPLE 18

Photopolymerization Using Thioxanthone/Amine/Maleimide Formulations

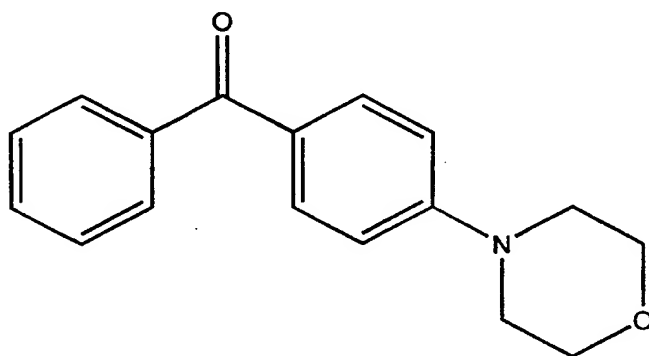
Additional studies examined the use of benzophenone derivatives, and in particular thioxanthone derivatives, to sensitize initiation by maleimides. Three types of experiments were performed using N-methyl maleimide and a variety of

thioxanthone photoinitiators. Specific thioxanthenes (available from First Chemical Corporation) include isopropyl thioxanthone (ITX), LTX having the formula

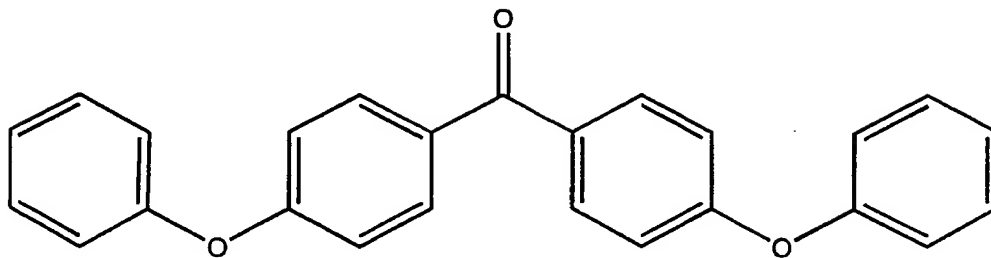


4-morpholinobenzophenone (XPI-115) having the formula

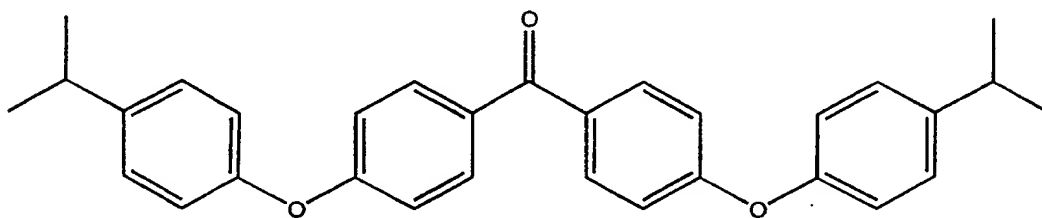
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4,4'-diphenoxybenzophenone (XPI-113) having the formula



5 and XPI-133 having the formula



First, formulations with various photoinitiators were prepared containing HDDA and NMDEA, with and without MMI. These formulations were then tested by photo-differential scanning calorimetry (photo-DSC), using a Xenon-doped mercury lamp at 25°C using (1) a 313 nm band pass filter, (2) a 365 nm band pass filter, and (3) the full arc of the lamp at different intensities.

313 nm Band Pass Filter (BPF) Experiments

15 At 313 nm, both the maleimide and the photoinitiator absorb photons, with the relative absorbance depending of the ratio of the respective molar extinction coefficients. Formulations were prepared to have equal absorbance of different benzophenone derivatives at 313 nm. The experiments were performed in nitrogen, with a filtered light intensity of about 1 mW/cm².

20 The data in Table 1 show that when the maleimide is used in conjunction with ITX and XPI-115 at these concentrations and under these conditions, the average peak exotherm maximum (polymerization rate) is enhanced. Also,

enhanced relative conversions are obtained when the maleimide is used in conjunction with ITX, XPI-113, XPI-115, and XPI-133.

Table 1

Data from 313 nm BPF Photo-DSC Experiments Using HDDA			
Photoinitiator	Formulation (mol% of compound)	Average Exotherm Peak Maximum (W/g)	Average Exotherm Integration (J/g)
ITX	0.080% ITX 0.86% MDEA	28.32	554.35
	0.080% ITX 1.2% MDEA 0.66% MMI	68.32	579.79
LTX	0.0113% LTX 1.07% MDEA	21.3	481.93
	0.0113% LTX 0.974% MDEA 0.608% MMI	12.8	470.1
XPI-113	0.013% XPI-113 1.09% MDEA	20.69	469.38
	0.012% XPI-113 1.09% MDEA 0.56% MMI	15.99	504.39
XPI-115	0.0025% XPI-115 1.18% MDEA	24.42	481.9
	0.0025% XPI-115 1.07% MDEA 0.63% MMI	29.59	489.51
XPI-133	0.0056% XPI-133 1.02% MDEA	16.17	435.63
	0.0055% XPI-133 1.03% MDEA 0.607% MMI	10.63	470.66

5

365 nm BPF Experiments

A second set of photo-DSC experiments were performed which were similar to those reported above except that a 365 nm band pass filter was used in place of the 313 nm band pass filter. At 365 nm, the principle absorbing species in these formulations should be the photoinitiator. Exotherm data from these experiments are shown below in Table 2.

10

Table 2

Data from 365 nm BPF Photo-DSC Experiments Using HDDA			
Photoinitiator	Formulation (mol% of compound)	Average Exotherm Peak Maximum (W/g)	Average Exotherm Integration (J/g)
ITX	0.090% ITX 0.942% MDEA	18.13	447.69
	0.090% ITX 1.0% MDEA 0.62% MMI	63.45	521.39
LTX	0.013% LTX 1.07% MDEA	23.77	508.91
	0.0113% LTX 0.974% MDEA 0.608% MMI	42.96	509.14

At these concentrations and under these conditions, there is dramatic enhancement of the maximum rates of polymerization when the maleimide is used in conjunction with ITX as well as with LTX. There is also enhancement of the relative conversion when the maleimide is included in the formulations. Absolute comparisons between ITX and LTX should not be made using this data, as the formulations were not prepared with equal photoinitiator absorption at 365 nm.

Full Arc Experiments

Two formulations of HDDA with ITX, MDEA, with and without MMI were also tested using the full arc of the lamp at three different intensities, in nitrogen and in air. Peak exotherm maxima are listed below in Table 3. In nitrogen, at low intensity (30 mW/cm²), the formulation with the maleimide is approximately twice as efficient as that without. As the intensity increases to 100 and 300 mW/cm², the ratio between with maleimide and without decreases, while the absolute peak exotherm values continue to increase, as expected. In air, at 30 mW/cm², there is little difference between the exotherms of the two formulations. However, as the intensity increases to 100 and 300 mW/cm², the ratio (with MMI/without MMI) goes from 1.06 to 1.12 to 1.34, and the exotherm peak values get larger.

Table 3

Data from full arc photo-DSC experiments with HDDA			
Formulation (mol% of compound)	Light Intensity (mW/cm ²)	Exotherm Peak Maximum (W/g)	
		Nitrogen	Air
0.090% ITX 0.942% MDEA	30	50	39
	100	73	64
	300	97	77
0.090% ITX 1.0% MDEA 0.61% MMI	30	-	41
	100	97	80
	300	129	104

Short Duration Irradiation Photo-DSC Experiments

- 5 To investigate the performance of sensitized maleimide-acrylic formulations in air a third battery of experiments was performed using formulations of HDDA, MDEA, and ITX, and with and without methyl maleimide. These photo-DSC experiments were performed at 25°C in nitrogen and in air with 1 second irradiation times using a shuttered xenon-doped mercury light source.
- 10 The experiments were conducted in the absence of a filter, in nitrogen and in air, at light intensities from 30 to 750 mW/cm². Three formulations were tested containing HDDA, MDEA, and ITX, with and without MMI. Representative exotherm peak maxima and exotherm integration values are shown below in Table 4.

Table 4

Data from 1-Second Exposure Photo-DSC Experiments with HDDA and ITX						
Light Intensity (mW/cm ²)	Formulations (mol % of compound)					
	0.090% ITX 0.942% MDEA		0.090% ITX 1.0% MDEA 0.62% MMI		0.0090% ITX 1.01% MDEA 0.0806% MMI	
	Peak Maximu m (W/g)	Peak Integral (J/g)	Peak Maximu m (W/g)	Peak Integral (J/g)	Peak Maximu m (W/g)	Peak Integral(J/ g)
Values in Nitrogen						
30	10.25	55.30	31.63	155.97	58.57	272.24
100	25.61	108.70	77.16	400.42	104.95	477.98
300	51.06	216.73	111.13	531.72	122.04	524.88
500	66.52	317.29	117.97	545.81	-	-
750	93.68	414.60	135.31	564.38	-	-
Values in Air						
30	9.29	36.49	2.21	9.34	14.54	55.71
100	23.26	91.58	30.90	132.60	65.20	281.53
300	38.91	170.58	100.60	429.47	111.87	449.55
500	57.56	242.04	115.17	475.92	-	-
750	-	-	124.72	510.68	-	-

From this data, it can be clearly observed that in nitrogen, at all intensities
 5 and at both concentrations of MMI, the formulations containing maleimide perform much
 better than the HDDA formulation with only ITX and amine.

Another useful comparison is that between the sensitized
 maleimide/ITX/amine initiating system and a typical conventional alpha-cleavage type
 photoinitiator. A short set of experiments was performed using one of the sensitized
 10 maleimide containing formulations from above and an HDDA formulation which
 contained 2,2-dimethoxy-2-phenylacetophenone (known commercially as BDK and

Irgacure 651). These photo-DSC runs were conducted at 25°C in nitrogen, at 100 mW/cm² on-sample light intensity, with a one second exposure time. Photo-DSC exotherm values are given below in Table 5. The sensitized maleimide-containing formulation gave a peak maximum on average about 69% of the peak maximum obtained with the Irgacure 651 formulation. The relative double bond conversion for the sensitized maleimide initiated formulations was about 79% of that obtained when the conventional alpha-cleavage photoinitiator was used. It is interesting to note that there is 0.97 weight percent initiator in the case of the Irgacure 651/HDDA formulation, but only 0.59 weight percent of initiating system in the maleimide/ITX/MDEA/HDDA formulation.

Table 5

Photo-DSC Exotherm Values Comparing Maleimide/ITX/MDEA to IC651 in HDDA		
Formulation (mol% of compound)	Average Exotherm Peak Maximum (W/g)	Average Exotherm Peak Integration (J/g)
0.0090% ITX 1.01% MDEA 0.0806% MMI	108.37	489.36
0.86% Irgacure 651	156.70	622.82

Sensitization of Aromatic Maleimides

Experiments were also performed to determine if initiation of acrylic systems via sensitized aromatic maleimides is possible. Formulations were prepared using HDDA, ITX, and MDEA with several aromatic maleimides. The aromatic maleimides used in these experiments are N-phenylmaleimide (PMI), N-(2-trifluoromethylphenyl)maleimide (2CF3PMI), N-(2-t-butylphenyl)maleimide (2tBPMI), and α -methyl-N-(2-trifluoromethyl phenyl)maleimide (2CF3PCI). Photo-DSC experiments were conducted in nitrogen at 25°C using a medium pressure mercury lamp fitted with a 365 nm band pass filter, with an unfiltered on-sample light intensity of 28 mW/cm². Exotherm peak maxima are listed below in Table 6. The data demonstrates that aromatic maleimides can be "sensitized" (again, though sensitization has not been proven mechanistically) using ITX in acrylic systems. Also very significant is that the aromatic maleimides are not required to be "twisted" (as in the initiation of acrylic

systems by direct excitation of the maleimide), as N-phenyl maleimide appears to have the same synergistic effect.

Table 6

Photo-DSC Peak Maxima for ITX/MDEA/Arylmaleimides in HDDA					
Formulation (mol% of compound)	0.040% ITX 1.00% MDEA	0.040% ITX 0.976% MDEA 0.309% PMI	0.040% ITX 0.996% MDEA 0.311% 2CF3PMI	0.040% ITX 1.03% MDEA 0.313% 2tBPMI	0.040% ITX 1.04% MDEA 0.325% 2CF3PCI
Exotherm Peak Maximum (W/g)	12	34	40	42	46

In summary, the data reported herein show that a dramatic synergistic effect occurs when N-aliphatic and N-aromatic maleimides are used in conjunction with benzophenone/thioxanthone photoinitiators in the presence of an amine hydrogen atom-donor in hexanedioldiacrylate. Although not wishing to be bound by any explanation of the invention, this effect likely occurs through excitation of the conventional photoinitiator followed by energy transfer to the maleimide, which then hydrogen-atom abstracts and initiates free-radical polymerization. Both aliphatic and aromatic maleimides appear to exhibit the synergism, and the aromatic maleimides are not required to be "twisted" (the phenyl ring out of plane with respect to the maleimide ring). Specifically, synergism leading to enhanced rates of cure and enhanced conversions has been observed when N-methylmaleimide is used at low concentrations in conjunction with benzophenone, ITX, LTX, and XPI-115. Enhanced conversions are also noted when MMI is used in conjunction with XPI-113 and XPI-133. Similar results have been observed using N-aromatic maleimides including N-phenylmaleimide, N-(2-trifluoromethylphenyl)maleimide, N-(2-t-butyl phenyl) maleimide, and α -methyl-N-(2-trifluoromethyl phenyl)maleimide. Under conditions designed to begin to simulate industrial curing conditions, sensitized maleimide-containing acrylic formulations were observed to have higher rates of cure and higher relative conversions in air than the same formulations without the maleimide in nitrogen.

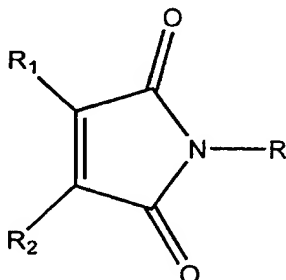
The foregoing examples are illustrative of the present invention and are not to be construed as limiting thereof. Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

THAT WHICH IS CLAIMED IS:

1. A photopolymerizable composition comprising at least one
5 photopolymerizable compound having at least one ethylenically unsaturated double bond,
at least one maleimide compound, and at least one photoactive compound without a
maleimide functionality.

2. The composition of Claim 1, wherein said at least one maleimide
10 compound is selected from the group consisting of alkyl maleimides, functionalized
aliphatic maleimides, aromatic maleimides, maleimide, maleic anhydride, and mixtures
thereof.

3. The composition of Claim 2, wherein said maleimide compound
15 comprises an alkyl maleimide of the formula



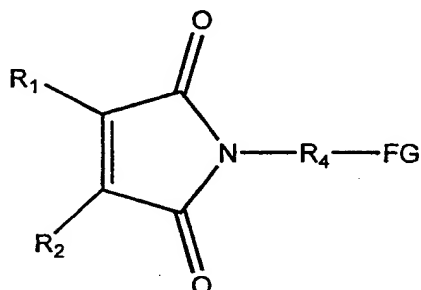
wherein:

each R₁ and R₂ is independently selected from the group consisting of
hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R₁ and R₂ together
20 form a fused substituted or unsubstituted saturated or unsaturated five or six membered
cyclic hydrocarbon or heterocyclic ring system; and

R is straight chain, branched or cyclic C1-C10 alkyl, optionally substituted
with one or more C1-C4 alkyl.

4. The composition of Claim 3, wherein said alkyl maleimide is selected from the group consisting of methyl maleimide, hexyl maleimide, cyclohexyl maleimide, and mixtures thereof.

5. The composition of Claim 2, wherein said functionalized aliphatic maleimide comprises a compound of the formula:



wherein:

(a) each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system;

(b) R_4 is linear or branched C1 to C10 alkyl, heteroatom, or silicon -SiH₂-; and

(c1) when R_4 is C1 to C10 alkyl, FG is a functional group selected from the group consisting of -OR₃, -SR₃, -SiH₂R₃, -OC(O)N(R₃)₂, -OC(O)C(=CHR₃)R₃, -OC(O)R₃, -C(O)R₃, -N(R₃)₂, -C(O)OR₃, -NCO, -C(O)N(R₃)₂, -OC(O)OR₃, -CN, halogen, -CH₂N-aryl-FG', -CH₂N-aryl-R₃-FG', sulfonic acid, quaternary ammonium, and salts thereof, in which each R₃ is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl, and in which FG' is selected from the group consisting of -OR₃, -SR₃, -SiH₂R₃, -OC(O)N(R₃)₂, -OC(O)C(=CHR₃)R₃, -OC(O)R₃, -C(O)R₃, -N(R₃)₂, -C(O)OR₃, -NCO, -C(O)N(R₃)₂, -OC(O)OR₃, -CN, halogen, sulfonic acid, and quaternary ammonium, or

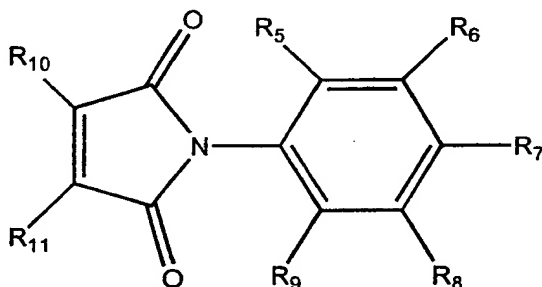
(c2) when R_4 is a heteroatom or silicon $-\text{SiH}_2-$, FG is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, alkylaryl, arylalkyl, alkyl-FG'', and aryl-FG'', wherein FG'' is the same as FG' as defined in (c1) above, or

(c3) FG is a functional group as defined in (c1) in combination with a
 5 spacer group linking said maleimide unit with at least one other maleimide unit to form a di- or multifunctional maleimide compound.

6. The composition of Claim 5, wherein said functionalized aliphatic maleimide is selected from the group consisting of hydroxy methylmaleimide, hydroxy ethylmaleimide, triethylene glycol biscarbonate bisethylmaleimide, 2-ethylcarbonate ethylmaleimide, 2-isopropyl urethane ethylmaleimide, 2-acryloyl ethylmaleimide, acetoxymethyl maleimide, isophorone bisurethane bisethylmaleimide, bisethylmaleimide carbonate, 4,9-dioxo-1,12 dodecane bismaleimide, bispropyl maleimide, dodecane N,N' -bismaleimide, and mixtures thereof.

15

7. The composition of Claim 2, wherein said aromatic maleimide comprises a compound of the formula



wherein:

20 each of R_5 , R_6 , R_7 , R_8 , and R_9 is independently selected from the group consisting of H, CX_3 , COOR_{12} , COR_{12} , OR_{12} , CN, SR_{12} , $\text{N}(\text{R}_{12})_2$, R_{13} , X, and MI;

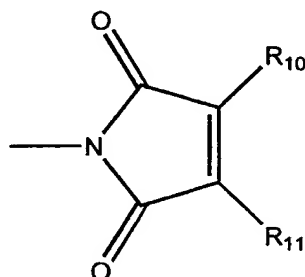
R_{10} and R_{11} each is independently selected from the group consisting of H, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic
 25 hydrocarbon or heterocyclic ring system;

X is halide;

R₁₂ is selected from the group consisting of H, lower alkyl, cycloalkyl, and aryl;

R₁₃ is selected from the group consisting of lower alkyl, cycloalkyl, and aryl, or R₁₃ is a spacer group connecting at least two compounds of the above formula to form a di- or multi-functional maleimide; and

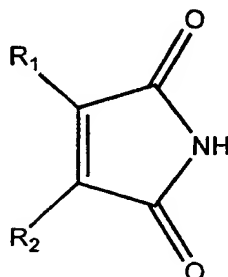
MI is



wherein R₁₀ and R₁₁ are as defined above.

8. The composition of Claim 7, wherein said aromatic maleimide is selected from the group consisting of phenyl maleimide, N-(2-CF₃-phenyl)maleimide, N-(2-t-butylphenyl)maleimide, N-(2-CF₃-phenyl)methylmaleimide, N-(2,4,6-isopropyl-3-maleimide phenyl)maleimide, N-(2-iodophenyl)maleimide, N-(2-bromo-3,5-CF₃-phenyl)maleimide, di(4-maleimido phenyl)methane, N-(2-chlorophenyl) maleimide, N-(2-bromophenyl) maleimide, N-(2-fluorophenyl) maleimide, N-(4-CF₃-phenyl) maleimide, di(3, 5-diethyl-4-maleimidophenyl)methane, and mixtures thereof.

9. The composition of Claim 2, wherein said maleimide compound comprises a maleimide compound of the formula

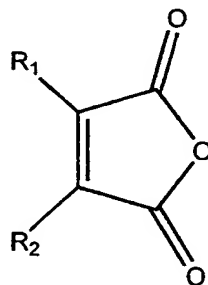


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wherein each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system.

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10. The composition of Claim 2, wherein said maleimide compound comprises maleimide anhydride of the formula

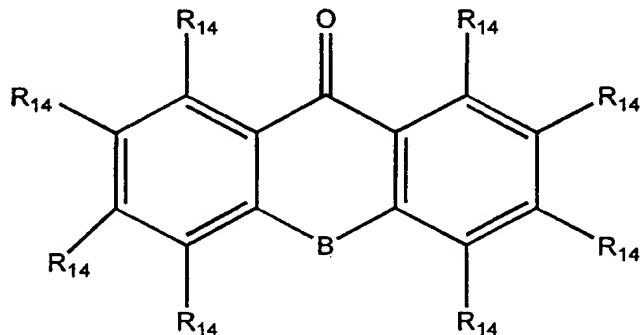


wherein each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system.

15

11. The composition of Claim 1, wherein said at least one photoactive compound without a maleimide functionality comprises a benzophenone compound.

12. The composition of Claim 11, wherein said benzophenone



5 compound comprises a compound of the formula

wherein:

B is (H,H), -CH₂-, -S-, -O-, -CO-, -NR₁₅-, or a bond bridging the two aromatic rings;

10 each R₁₄ is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, aryl, alkylaryl, arylalkyl, halogen, trihaloalkyl, -CN, -NO₂, -C(O)OR₁₅, -C(O)R₁₅, -OR₁₅, -N(R₁₅)₂, -OC(O)CR₁₅=CHR₁₅, R₁₆, -OR₁₆, -R₁₇-OC(O)CR₁₅=CHR₁₅, polymerizable moieties, and oligomeric and polymeric moieties;

15 R₁₅ is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl;

R₁₆ is one or more saturated or unsaturated five or six membered hydrocarbon or heterocyclic ring system, optionally substituted with one or more alkyl, cycloalkyl, or halogen; and

20 R₁₇ is selected from the group consisting of alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl.

13. The composition of Claim 11, wherein said benzophenone compound is selected from the group consisting benzophenone, thioxanthone, isopropylthioxanthone, chloroxanthone, 4-morpholinobenzophenone, 4,4'-

diphenoxybenzophenone, methyl o-benzoylbenzoate, 1-methyl-2-(2-ethylhexyloxy)thioxanthone, 4,4'-di-(4-isopropylphenoxy)benzophenone, acrylic acid 4-benzoylphenyl ester, 4,4'-diphenylbenzophenone, 4-phenylbenzophenone, and mixtures thereof.

5

14. The composition of Claim 1, wherein said at least one photopolymerizable compound is selected from the group consisting of monomers and oligomers derived from acrylic and methacrylic acid, optionally dispersed or dissolved in a solvent that is copolymerizable therewith.

10

15. The composition of Claim 14, wherein said photopolymerizable compound is selected from the group consisting of methyl acrylate, ethyl acrylate, n- or tert-butylacrylate, isooctyl acrylate, methyl methacrylate, ethylmethacrylate, 2-ethylhexyl methacrylate, butylacrylate, isobutyl methacrylate, hydroxy acrylates, glycol acrylates, allyl acrylates, epoxy acrylates, aminoplast acrylates, acrylated epoxides, acrylated polyesters, acrylated polyurethanes, and mixtures thereof.

15

16. The composition of Claim 1, wherein said composition further comprises at least one hydrogen atom donor compound.

20

17. The composition of Claim 1, wherein said hydrogen atom donor compound comprises a tertiary amine.

18. The composition of Claim 1, wherein said photopolymerizable compound comprises a hydrogen atom donor molecular component.

25

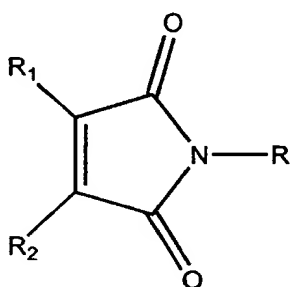
19. The composition of Claim 1, comprising said maleimide compound in an amount of about 0.01 to about 2 mole percent.

20. A method of polymerizing a polymerizable compound having at least one ethylenically unsaturated double bond, comprising exposing said compound to

radiation in the presence of at least one maleimide compound and at least one photoactive compound without a maleimide functionality.

21. The method of Claim 20, wherein said at least one maleimide compound is selected from the group consisting of alkyl maleimides, functionalized aliphatic maleimides, aromatic maleimides, maleimide, maleic anhydride, and mixtures thereof.

22. The method of Claim 21, wherein said maleimide compound comprises an alkyl maleimide of the formula



wherein:

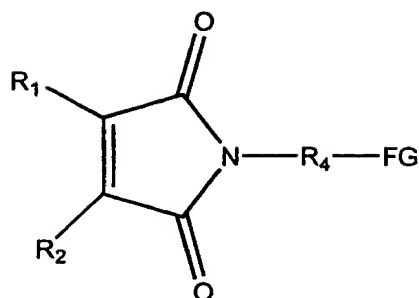
10 each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system; and

15 R is straight chain, branched or cyclic C1-C10 alkyl, optionally substituted with one or more C1-C4 alkyl.

23. The method of Claim 22, wherein said alkyl maleimide is selected from the group consisting of methyl maleimide, hexyl maleimide, cyclohexyl maleimide, and mixtures thereof.

20

24. The method of Claim 21, wherein said functionalized aliphatic maleimide comprises a compound of the formula:



wherein:

(a) each R_1 and R_2 is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system;

(b) R_4 is linear or branched C1 to C10 alkyl, heteroatom, or silicon $-\text{SiH}_2-$; and

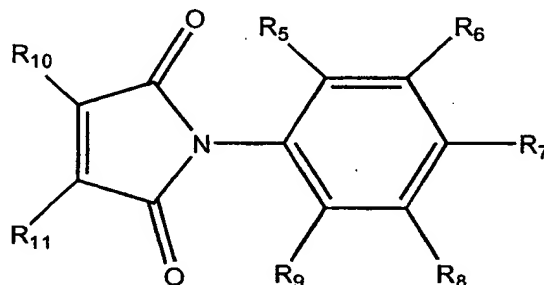
(c1) when R_4 is C1 to C10 alkyl, FG is a functional group selected from the group consisting of $-\text{OR}_3$, $-\text{SR}_3$, $-\text{SiH}_2\text{R}_3$, $-\text{OC}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{C}(=\text{CHR}_3)\text{R}_3$, $-\text{OC}(\text{O})\text{R}_3$, $-\text{C}(\text{O})\text{R}_3$, $-\text{N}(\text{R}_3)_2$, $-\text{C}(\text{O})\text{OR}_3$, $-\text{NCO}$, $-\text{C}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{OR}_3$, $-\text{CN}$, halogen, $-\text{CH}_2\text{N-aryl-FG}'$, $-\text{CH}_2\text{N-aryl-R}_3\text{-FG}'$, sulfonic acid, quaternary ammonium, and salts thereof, in which each R_3 is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl, and in which FG' is selected from the group consisting of $-\text{OR}_3$, $-\text{SR}_3$, $-\text{SiH}_2\text{R}_3$, $-\text{OC}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{C}(=\text{CHR}_3)\text{R}_3$, $-\text{OC}(\text{O})\text{R}_3$, $-\text{C}(\text{O})\text{R}_3$, $-\text{N}(\text{R}_3)_2$, $-\text{C}(\text{O})\text{OR}_3$, $-\text{NCO}$, $-\text{C}(\text{O})\text{N}(\text{R}_3)_2$, $-\text{OC}(\text{O})\text{OR}_3$, $-\text{CN}$, halogen, sulfonic acid, and quaternary ammonium, or

(c2) when R_4 is a heteroatom or silicon $-\text{SiH}_2-$, FG is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, alkylaryl, arylalkyl, alkyl- FG'' , and aryl- FG'' , wherein FG'' is the same as FG' as defined in (c1) above, or

(c3) FG is a functional group as defined in (c1) in combination with a spacer group linking said maleimide unit with at least one other maleimide unit to form a di- or multifunctional maleimide compound.

25. The method of Claim 24, wherein said functionalized aliphatic maleimide is selected from the group consisting of hydroxy methylmaleimide, hydroxy ethylmaleimide, triethylene glycol biscarbonate bisethylmaleimide, 2-ethylcarbonate ethylmaleimide, 2-isopropyl urethane ethylmaleimide, 2-acryloyl ethylmaleimide, 5 acetoxymethyl maleimide, isophorone bisurethane bisethylmaleimide, bisethylmaleimide carbonate, 4,9-dioxo-1,12 dodecane bismaleimide, bispropyl maleimide, dodecane N,N'-bismaleimide, and mixtures thereof.

26. The method of Claim 21, wherein said aromatic maleimide 10 comprises a compound of the formula



wherein:

each of R₅, R₆, R₇, R₈, and R₉ is independently selected from the group consisting of H, CX₃, COOR₁₂, COR₁₂, OR₁₂, CN, SR₁₂, N(R₁₂)₂, R₁₃, X, and MI;

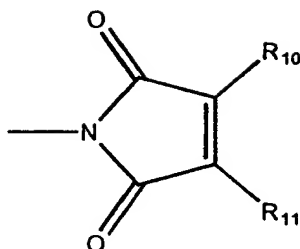
15 R₁₀ and R₁₁ each is independently selected from the group consisting of H, C₁ to C₁₀ alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R₁ and R₂ together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system;

X is halide;

20 R₁₂ is selected from the group consisting of H, lower alkyl, cycloalkyl, and aryl;

R₁₃ is selected from the group consisting of lower alkyl, cycloalkyl, and aryl, or R₁₃ is a spacer group connecting at least two compounds of the above formula to form a di- or multi-functional maleimide; and

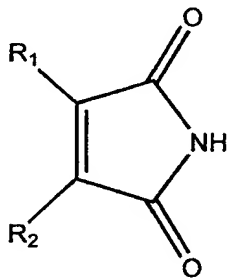
MI is



wherein R₁₀ and R₁₁ are as defined above.

- 5 27. The method of Claim 26, wherein said aromatic maleimide is selected from the group consisting of phenyl maleimide, N-(2-CF₃-phenyl)maleimide, N-(2-t-butylphenyl)maleimide, N-(2-CF₃-phenyl)methylmaleimide, N-(2,4,6-isopropyl-3-maloimide phenyl)maleimide, N-(2-iodophenyl)maleimide, N-(2-bromo-3,5-CF₃-phenyl)maleimide, di(4-maleimido phenyl)methane, N-(2-chlorophenyl) maleimide, N-
10 (2-bromophenyl) maleimide, N-(2-fluorophenyl) maleimide, N-(4-CF₃-phenyl) maleimide, di(3, 5-diethyl-4-maleimidophenyl)methane, and mixtures thereof.

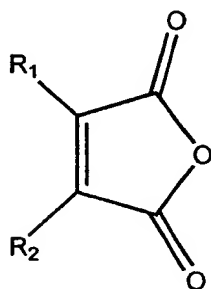
28. The method of Claim 21, wherein said maleimide compound comprises a maleimide compound of the formula



- 15 wherein each R₁ and R₂ is independently selected from the group consisting of hydrogen, C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R₁ and R₂ together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system.

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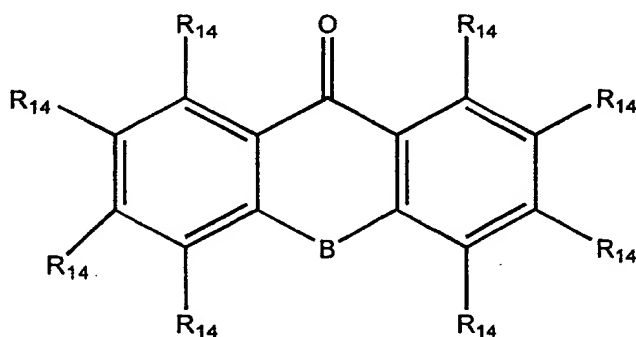
29. The method of Claim 21, wherein said maleimide compound comprises maleimide anhydride of the formula



wherein each R_1 and R_2 is independently selected from the group consisting of hydrogen,
 5 C1 to C10 alkyl, cycloalkyl, aryl, alkoxy, and halogen, or R_1 and R_2 together form a fused substituted or unsubstituted saturated or unsaturated five or six membered cyclic hydrocarbon or heterocyclic ring system.

30. The method of Claim 20 wherein said at least one photoactive
 10 compound without a maleimide functionality comprises a benzophenone compound.

31. The method of Claim 30, wherein said benzophenone compound has the formula



wherein:

15 B is (H,H), $-CH_2-$, $-S-$, $-O-$, $-CO-$, $-NR_{15}-$, or a bond bridging the two aromatic rings;

each R_{14} is independently selected from the group consisting of hydrogen, alkyl, cycloalkyl, alkoxy, aryl, alkylaryl, arylalkyl, halogen, trihaloalkyl, -CN, -NO₂, -C(O)OR₁₅, -C(O)R₁₅, -OR₁₅, -N(R₁₅)₂, -OC(O)CR₁₅=CHR₁₅, R₁₆, -OR₁₆, -R₁₇-OC(O)CR₁₅=CHR₁₅, polymerizable moieties, and oligomeric and polymeric moieties;

5 R_{15} is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl;

R_{16} is one or more saturated or unsaturated five or six membered hydrocarbon or heterocyclic ring system, optionally substituted with one or more alkyl, cycloalkyl, or halogen; and

10 R_{17} is selected from the group consisting of alkyl, aryl, cycloalkyl, arylalkyl, and alkylaryl.

32. The method of Claim 30, wherein said benzophenone compound is selected from the group consisting benzophenone, thioxanthone, isopropylthioxanthone, 15 chlorothioxanthone, 4-morpholinobenzophenone, 4,4'-diphenoxybenzophenone, methyl o-benzoylbenzoate, 1-methyl-2-(2-ethylhexyloxy)thioxanthone, 4,4'-di-(4-isopropylphenoxy)benzophenone, acrylic acid 4-benzoylphenyl ester, 4,4'-diphenylbenzophenone, 4-phenylbenzophenone, and mixtures thereof.

20 33. The method of Claim 20, wherein said at least one photopolymerizable compound is selected from the group consisting of monomers and oligomers derived from acrylic and methacrylic acid, optionally dispersed or dissolved in a solvent that is copolymerizable therewith.

25 34. The method of Claim 33, wherein said photopolymerizable compound is selected from the group consisting of methyl acrylate, ethyl acrylate, n- or tert-butylacrylate, isooctyl acrylate, methyl methacrylate, ethylmethacrylate, 2-ethylhexyl methacrylate, butylacrylate, isobutyl methacrylate, hydroxy acrylates, glycol acrylates, allyl acrylates, epoxy acrylates, aminoplast acrylates, acrylated epoxides, acrylated 30 polyesters, acrylated polyurethanes, and mixtures thereof.

35. The method of Claim 20, wherein said composition further comprises a hydrogen atom donor compound.

36. The method of Claim 35, wherein said hydrogen atom
5 donor comprises a tertiary amine.

37. The method of Claim 20, wherein said photopolymerizable compound comprises a hydrogen atom donor molecular component.

38. The method of Claim 20, wherein said maleimide compound is present in an amount of about 0.01 to about 2 mole percent.

1/5

MMI & BENZOPHENONE EFFECT ON THE POLYMERIZATION
1%NMDEA IN HDODA, MEDIUM PRESSURE Hg LIGHT
40°C, 1 MINUTE N₂ PURGE, 2ul, 29.06W/cm²)

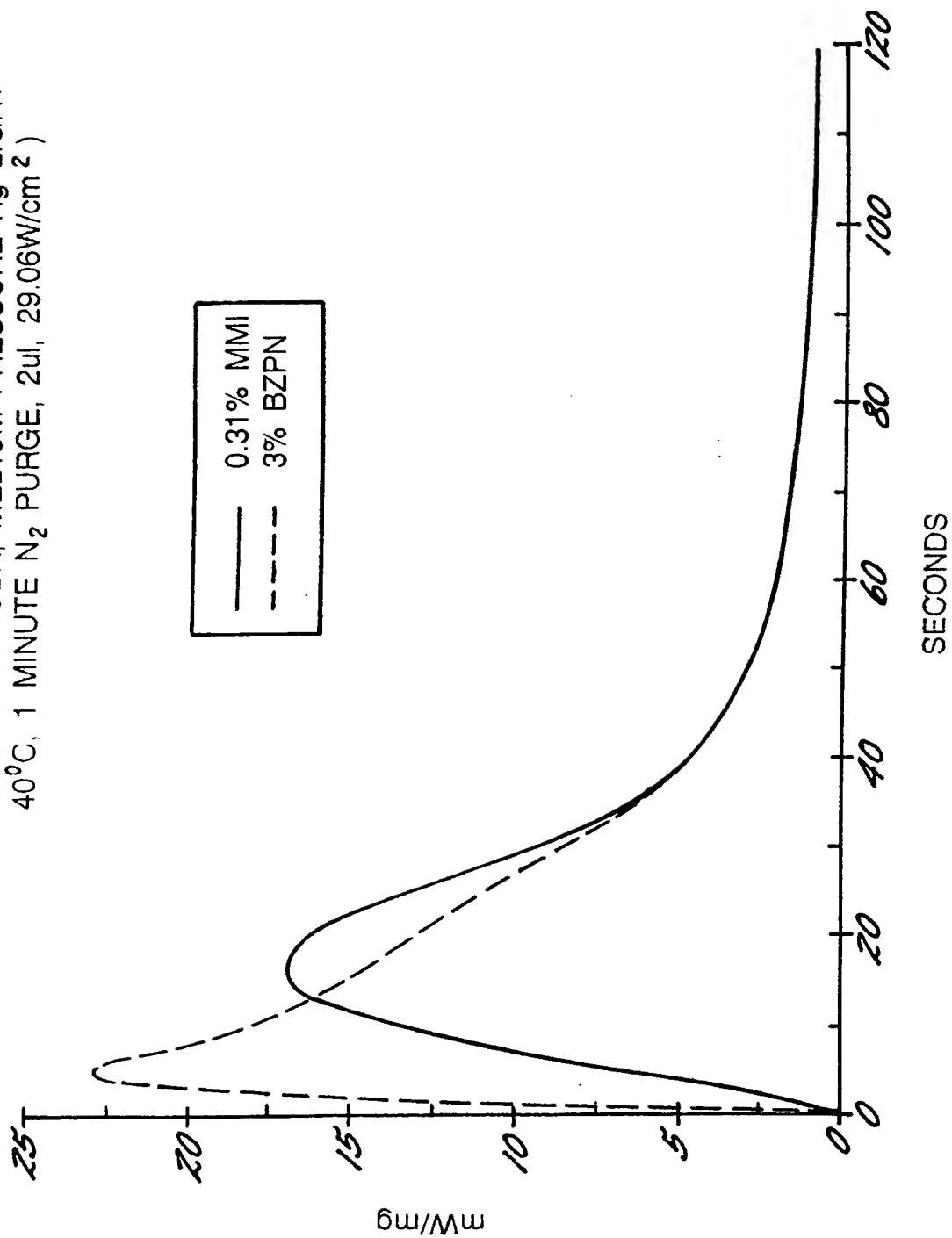


FIG. 1.

2/5

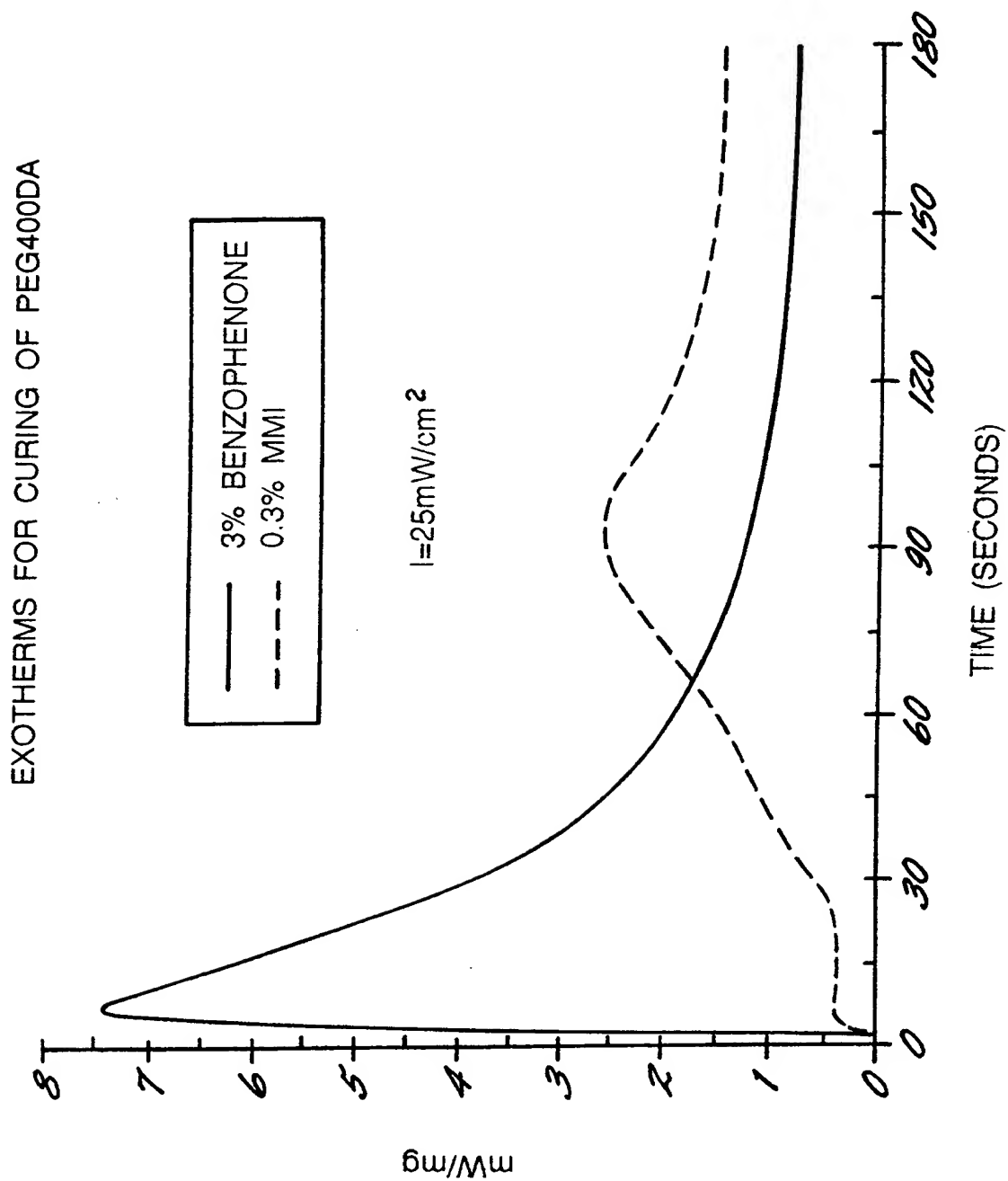


FIG. 2.

MMI & BENZOPHENONE EFFECT ON THE POLYMERIZATION
1%NMDEA IN HDODA, MEDIUM PRESSURE HgLIGHT(LS95.ORG)
40°C, 1 MINUTE N₂ PURGE, 2ul, 29.06mW/cm²

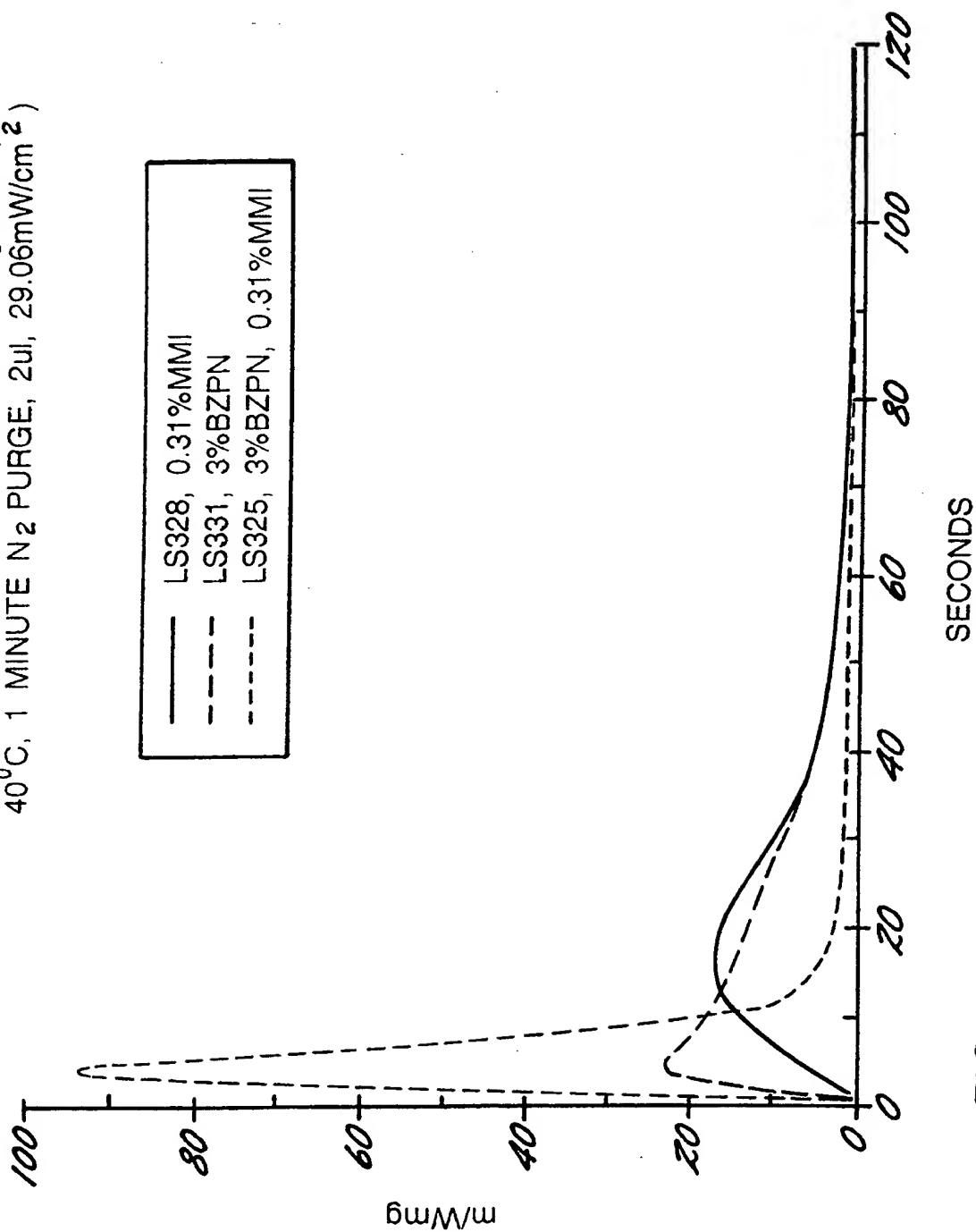


FIG. 3.

4/5

MMI & BENZOPHENONE EFFECT ON THE POLYMERIZATION

1%NMDEA, 3%BZPN IN HDODA, 365nm(LS116.ORG)

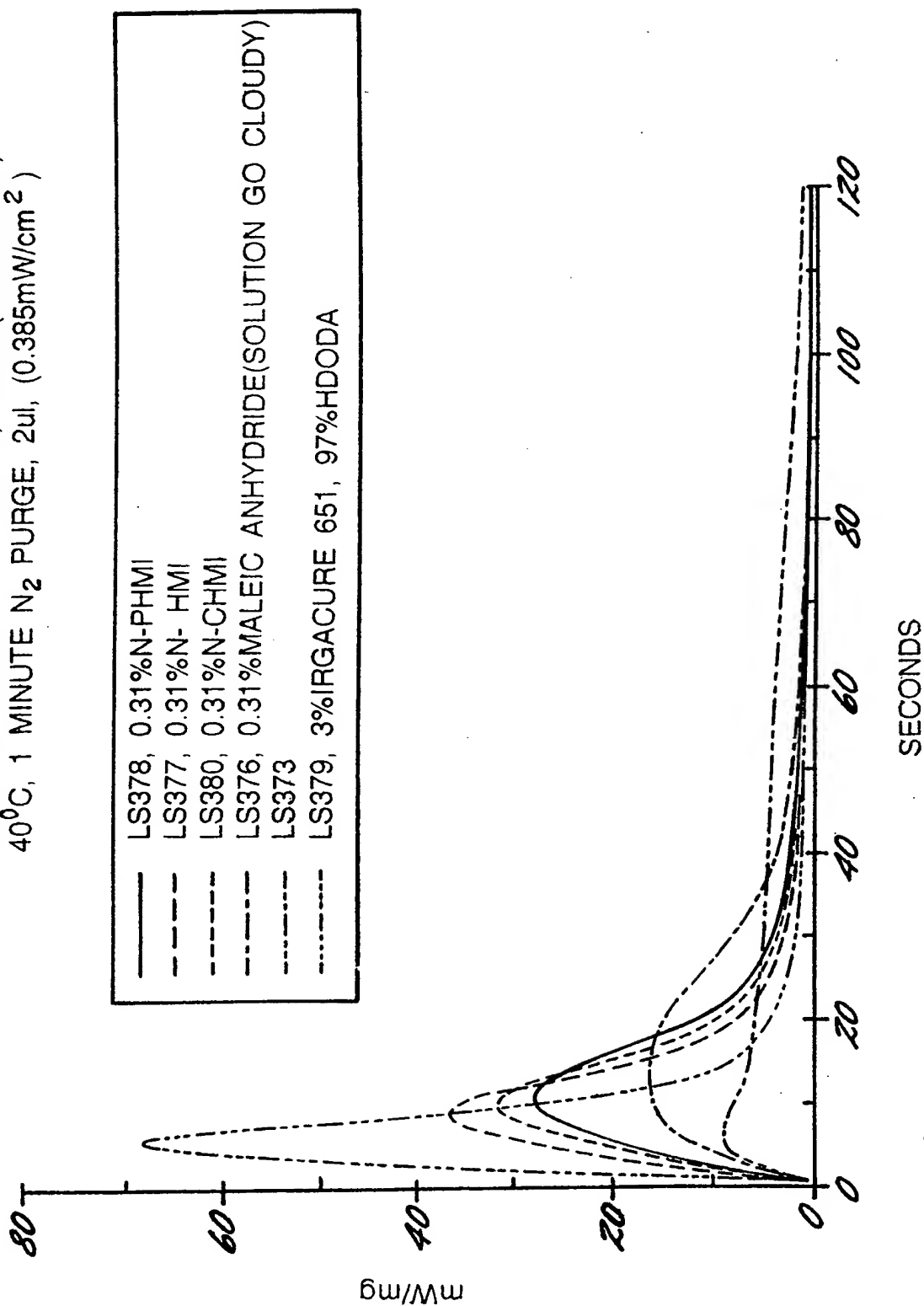
40°C, 1 MINUTE N₂ PURGE, 2ul, (0.385mW/cm²)

FIG. 4.

5/5

N-SUB-MALEIMIDE OR REPLACEMENT EFFECT
ON THE POLYMERIZATION
1%NMDEA, 3%BZPN IN HDODA, 365nm(LS123.ORG)
40°C, 1 MINUTE N₂ PURGE, 2ul, (0.362mW/cm²)

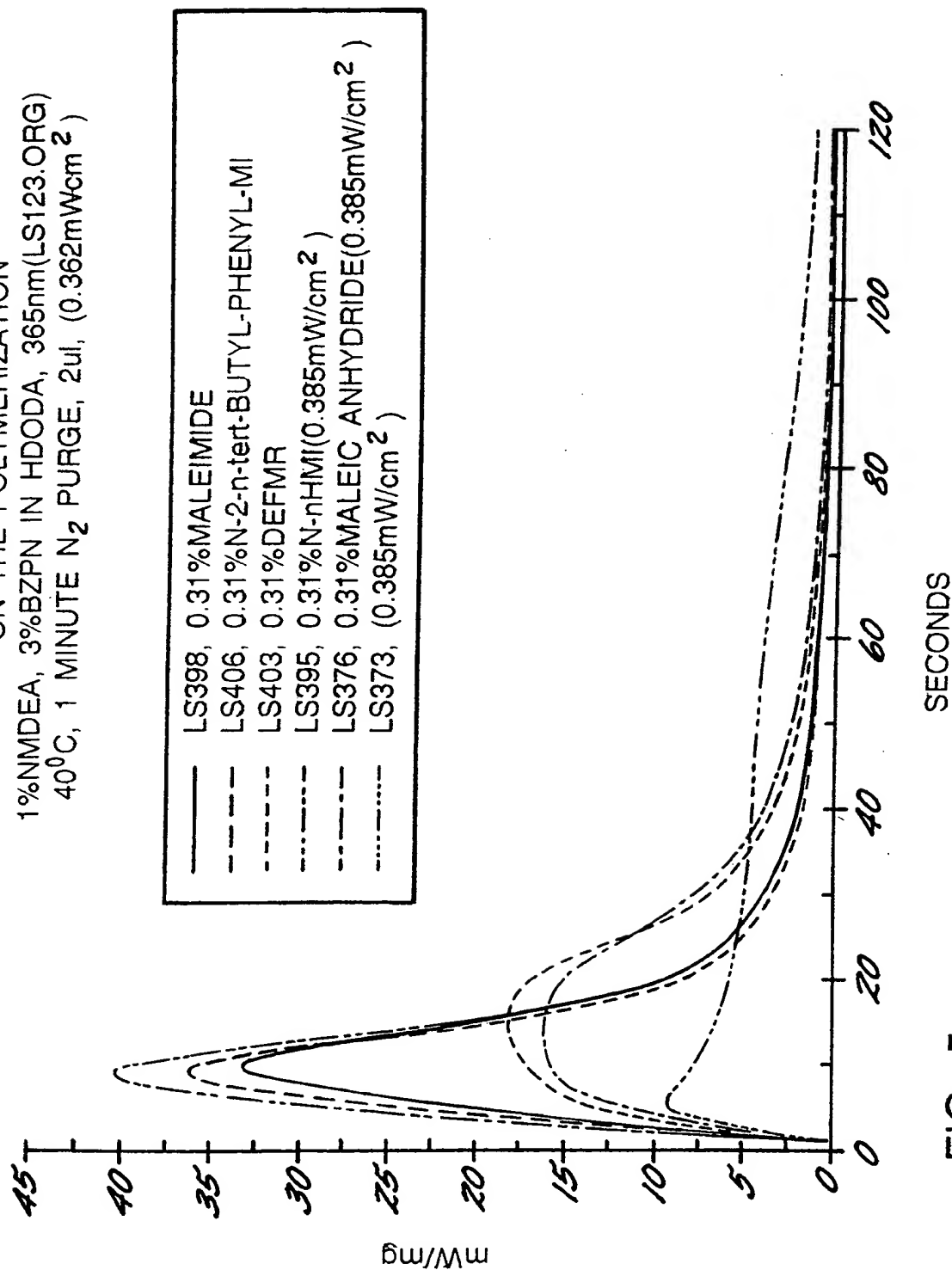


FIG. 5.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/01989

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03F7/031

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 304 174 A (IMPERIAL CHEMICAL INDUSTRIES PLC) 22 February 1989</p> <p>see page 3, line 15 - line 55 see page 4, line 1 - line 18 see page 5, line 15 see page 5, line 21 see page 5, line 22 see page 5, line 39 see examples</p> <p style="text-align: center;">--- -/--</p>	<p>1-8, 11-21, 24-27, 30-38</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 May 1999

Date of mailing of the international search report

21/05/1999

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INTERNATIONAL SEARCH REPORT

Int. J. Application No

PCT/US 99/01989

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 416 975 A (G.E. GREEN ET AL.) 22 November 1983</p> <p>see column 13, line 3 see column 13, line 9 see column 18; examples 1-5 ----</p>	<p>1-8, 11-21, 24-27, 30-38</p>
X	<p>FR 2 293 467 A (SIEMENS AKTIENGESELLSCHAFT) 2 July 1976</p> <p>see page 3, line 18 - line 33 see page 4, line 34 - line 37 see page 7; example 1 ----</p>	<p>1-8, 11-21, 24-27, 30-38</p>
X	<p>FR 2 438 282 A (ASAHI KASEI KOGYO KABUSHIKI KAISHA) 30 April 1980</p> <p>see page 12, line 11 - line 37 see page 13, line 1 - line 16 see page 17, line 17 - line 30 see page 27; example 3 -----</p>	<p>1-8, 11-21, 24-27, 30-38</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/01989

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